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TEXT-BOOKS OF CHEMICAL RESEARCH AND ENGINEERING.

THE THEORY OF EMULSIONS AND EMULSIFICATION

BY

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FOREWORD

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P. BLAKISTON'S SON & CO.

1012 WALNUT STREET

1923

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Printed in Great Britain.

PREFACE

THE growth of Colloid Chemistry within recent years has been both rapid and varied, and several well-known books are now available, dealing with general principles. The subject of emulsions, however, has so far received but little treatment in such works. This may be due, firstly, to the fact that the greater part of the quantitative work is of comparatively recent date ; and secondly, because several points of theory are still obscure, whilst a really sound, all-embracing theory of emulsions and emulsification is still incomplete. The great theoretical importance of emulsions and their exceptional industrial applications seem to merit a monograph which will serve to collect and review the work of the many investigators in this field. The present volume is an attempt in this direction.

To a certain extent the treatment has followed historical lines, particularly as regards the earlier work, but the chief aim has been to follow a logical line of development based on modern physico-chemical principles.

Technical applications of emulsions have only been introduced either as illustrating some particular laboratory method on a large scale, or because some important theoretical point is involved. One volume could not adequately treat of both the theoretical aspects and the manifold industrial applications practised to-day.

The summary of the literature made by Professor W. D. Bancroft in 1912–13 has been found most useful, and been fully utilised.

A bibliography has been compiled which is believed to contain references to every paper of importance dealing with emulsions, in the hope that it will serve a useful purpose for research workers in this field.

My best thanks are due to Professor F. G. Donnan, F.R.S.,

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for his encouragement, and for supplying the Foreword to this book.

To Messrs. W. G. and H. C. Eddy (Los Angeles) I am grateful for supplying information on the electrical treatment of emulsions, and for supplying two blocks illustrating this practice (Figs. 19 and 20). I am also indebted to Professor Donnan and the Chemical Society (London) for permission to reproduce Dr. Bhatnagar's photographs of emulsions (Fig. 10). My best thanks are also due to Messrs. Breil and Martel (Paris) for the loan of blocks illustrating the homogenisation of milk (Figs. 16, 17, 18), to Messrs. The De Laval Separator Company for the loan of the block illustrating a cream separator (Fig. 22), and to Messrs. Davis-Perrett, Ltd., for the loan of the block illustrating their electrical de-oiling plant (Fig. 21).

To Mr. H. W. Richards, B.Sc., and Mr. J. Deane I am indebted for the preparation of the various graphs and diagrams in a form suitable for this volume.

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FOREWORD

THE study of emulsions and emulsification is of very great theoretical and practical interest. From the standpoint of pure science it throws great light on the problems of surface tension, surface concentration and adsorption, surface films, electrical double layers, adsorption of ions, Brownian motion, and the general theory of disperse systems and colloids. The study of emulsions and emulsification is also of great importance in biological science, *e.g.*, the adsorption of fats, the permeability of membranes, etc.

When we consider industrial and applied science, it is remarkable how many subjects of interest and importance are dependent on a knowledge of the formation, behaviour, and stability of emulsions. In this connection one has only to think of milk (and "synthetic" milk), butter, margarine, the emulsions and ointments of pharmacy, emulsified disinfectants and lubricants, rubber latex, spraying fluids, soaps and other detergents, flotation processes, and a host of other things, in order to realise the extremely important *rôle* of emulsions in practical life. The engineer who wants to prevent emulsification of his lubricating oil, or to remove oil from his condensed water, is dependent on the physical chemistry of emulsions for the methods which he employs.

Dr. William Clayton presents an excellent account of the subject in this book. He is peculiarly fitted for the task which he has undertaken, both from his knowledge of physical chemistry and his practical and scientific acquaintance with the behaviour of emulsions in the manufacture of margarine. His book can be confidently recommended, not only to all students of physico-chemical science, but also to engineers, metallurgists, biologists, pharmacists, chemical manufacturers, dairy chemists, horticulturists, farmers, and many others too numerous to mention.

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THE THEORY OF EMULSIONS AND EMULSIFICATION

CHAPTER I

EMULSIONS AND EMULSIFYING AGENTS

An emulsion is a system containing two liquid phases, one of which is dispersed as globules in the other. That liquid which is broken up into globules is termed the dispersed phase, whilst the liquid surrounding the globules is known as the continuous phase or dispersing medium. The two liquids, which must be immiscible or nearly so, are frequently referred to as the internal and external phases respectively.

For two given liquids A and B two sets of emulsions are theoretically possible, depending upon whether A is dispersed in B, or *vice versâ*. Also, there is no *à priori* reason why emulsions of any desired concentration should not be made of either liquid in the other.[1]

Most of the early work on emulsions dealt with systems in which various oils were dispersed in water, this type of emulsion being known as the oil-in-water type. Ostwald,[2] in 1910, first drew real attention to the existence of two types of emulsions, pointing out that emulsions of equal volume concentrations, but of opposite types, *i.e.*, oil-in-water and water-in-oil, would possess very different properties. Emulsions of both types are now common not only in the laboratory, but in technical practice.

Two pure liquids, *e.g.*, an oil and water, when shaken together or otherwise agitated, will temporarily produce an emulsion,

[1] An extension of this to alloys has been made by Gillet (*J. Phys. Chem.*, **20**, 729 (1916); cf. also Bancroft, *Chem. Met. Eng.*, **26**, 391 (1922)).

[2] *Koll. Zeits.*, **6**, 103 (1910). Emulsions of water-in-oil were, however, mentioned by Saunders (*Pharm. J.*, **5**, 663 (1874)) and Gerrand (*ibid.*, **18**, 431 (1887)).

but as soon as agitation ceases the drops of the respective liquids (both liquids become subdivided) coalesce, and separation into layers occurs. By suitable treatment fairly stable emulsions of a pure oil in water may be obtained, but the concentration of the oil is very low indeed. Thus, engine condenser water frequently contains very fine oil globules, forming a stable emulsion in which the concentration of oil is about 1 in 10,000. If a little oil be boiled with water under a reflux condenser, a similar emulsion is obtained.[1] Such dilute emulsions, which closely correspond to colloidal suspensions, present certain interesting features, the discussion of which is reserved for the following chapter owing to the important theoretical considerations involved.

In order to prepare concentrated stable emulsions of either the oil-in-water or the water-in-oil type, besides the two liquids, a third substance is necessary, known as the emulsifier or emulsifying agent. On the nature of the emulsifying agent depends the type of emulsion promoted. Water-soluble colloidal substances promote emulsions of the oil-in-water type, whilst oil-soluble colloids promote the reverse type. The theory underlying this is treated in Chapter VI.

Some of the more important emulsifiers may now be mentioned, and also the particular emulsions for which they have been used. The more detailed discussion of the emulsions themselves will appear throughout the following pages in various connections.

Oil-in-water Emulsions.—Gelatin is an excellent emulsifying agent for oils of both glyceride and hydrocarbon character. Detailed studies on the emulsification of benzene in water by means of gelatin have been made by Briggs and Schmidt,[2] and by Holmes and Child.[3] Similar emulsions were prepared by Nugent,[4] whilst Clayton [5] obtained data on the emulsification of arachis and cottonseed oils in aqueous gelatin solutions.[6]

[1] Lewis, *Koll. Zeits.*, **4**, 211 (1909).
[2] *J. Phys. Chem.*, **19**, 484 (1915).
[3] *J. Amer. Chem. Soc.*, **42**, 2049 (1920).
[4] *Trans. Farad. Soc.*, **17**, 703 (1922).
[5] *Trans. Farad. Soc.*, **16**, Appendix, p. 26 (1921).
[6] No investigations have been made on the effect of the pH of gelatin solutions in relation to emulsification.

In the preparation of pharmaceutical [1] emulsions many reagents are used, *e.g.*, egg-yolk, saponin, gum acacia, gum tragacanth, casein and Irish moss. Special studies on these various emulsifiers have been made by Marshall [2] (acacia), Roon and Oesper [3] (gum tragacanth), Fischer and Hooker [4] (casein, starch, agar, albumins, gums, egg-yolk), and Haas [5] (Irish moss). Newman [6] prepared emulsions of benzene in water, using hæmoglobin, lacmoid, pepsin, peptone, or dextrin.[7] Bhatnagar [8] has studied emulsions of kerosene in water, using casein, albumin and lecithin as emulsifiers.

Formerly alkalies were considered good emulsifying agents for oils and fats, and patents have been obtained in this connection, *e.g.*, Na_2CO_3, for emulsifying fats,[9] and soluble silicates for preparing cod-liver oil emulsions up to 50 per cent. volume concentration.[10] Donnan,[11] in 1899, showed that alkalies are only efficient in this respect by virtue of their forming soaps with the free fatty acids present in oils and fats. Soaps are excellent emulsifiers for all kinds of oils and fats, and have found wide use in industrial processes. Pickering's [12] investigations on soaps as emulsifiers are classical in emulsion literature. Pickering found that potash soaps were more efficient than sodium soaps for emulsifying a paraffin oil. When 70 to 80 per cent. of paraffin or benzene was emulsified in an aqueous solution of a potash soap, very viscous emulsions resulted. Using 1 c.c. of 1 per cent. aqueous solution of potash soap, he succeeded in emulsifying 99 c.c. of paraffin oil, forming an oil-in-water emulsion which was quite white and as stiff as a blancmange. Similar concentrated emulsions were prepared by Newman, who found that, by gradually adding benzene and emulsifying after each addition, 99 c.c. of benzene could

[1] Remington, "Practice of Pharmacy," (1907), p. 1153.
[2] *Pharm. J.*, **28**, 257 (1909); cf. Palmer, *J. Am. Chem. Soc.*, **44**, 1529 (1922).
[3] *J. Ind. Eng. Chem.*, **9**, 156 (1917).
[4] "Fats and Fatty Degeneration" (1917).
[5] *Pharm. J.*, **106**, 485 (1921); cf. Huber, *Koll. Zeits.*, **30**, 20—31 (1922).
[6] *J. Phys. Chem.*, **18**, 45 (1914).
[7] Cf. Hamburg, Brit. Pat. 26390 (1913).
[8] *J. C. S.*, **119**, 1760 (1921).
[9] Ger. Pat. 2915164 (1914).
[10] Kramer, U.S. Pat. 1207936 (1916).
[11] *Zeits. phys. Chem.*, **31**, 42 (1899).
[12] *J. C. S.*, **91**, 2001 (1907).

be dispersed in 1 c.c. of water containing 0·05 gram of sodium oleate. The emulsion was like a stiff jelly, and remained stable for over six weeks. Ammonium oleate has been used by Huff [1] for preparing emulsions of heavy transformer oils in water. Various soaps are also used in making insecticide emulsions, *e.g.*, potassium oleate and stearate.[2] Investigations on soaps as emulsifiers have been carried out by White and Marden,[3] Shorter and Ellingworth,[4] Bhatnagar,[5] Hillyer,[6] and Lehner and Bishop.[7] Amongst other substances proposed as emulsifiers for promoting oil-in-water emulsions are condensed milk (used in pharmacy), sugar,[8] silver dichromate [9] (promotes emulsions of chloroform in water), amylene [10] (for emulsifying mineral oil in water), sodium salts of sulphonic acids [11] (for emulsifying mineral oils), glycerol,[12] rosin,[13] and sodium resinate.[14] Many patents have also been granted for the use of emulsifying agents in margarine manufacture,[15] wherein stable concentrated emulsions are of great importance.

Water-in-oil Emulsions.—Newman [16] found that unstable emulsions of water in benzene could be made by previously dissolving in the benzene such substances as crude rubber (0·2 per cent.), paraffin wax (2 per cent.), rosin (5 per cent.), or sulphur (concentrated solution). Unstable emulsions of water in carbon disulphide were promoted by spermacetin, guncotton, and barium oleate as emulsifiers. Newman also found that the oleates of Mg, Zn, Ni, or Ca promoted emulsions of benzene in water.

Water may be emulsified in linseed oil owing to the rosin

[1] *Chem. Met. Eng.*, **25**, 865 (1921).
[2] U.S. Pat. 1374755 (1921); U.S. Pat. 1168534 (1916); Brit. Pat. 160511 (1919).
[3] *J. Phys. Chem.*, **24**, 617 (1920).
[4] *Proc. Roy. Soc.*, **92** (A), 231 (1916).
[5] *J. C. S.*, **119**, 61 (1921).
[6] *J. Amer. Chem. Soc.*, **25**, 511 (1903).
[7] *J. Phys. Chem.*, **22**, 68 and 95 (1918).
[8] Marshall, *Pharm. J.*, **28**, 257 (1909); Fischer and Hooker, "Fats and Fatty Degeneration" (1917), pp. 31, 44.
[9] Hofmann, *Zeits. phys. Chem.*, **63**, 295 (1914).
[10] Parsons and Wilson, *J. Ind. Eng. Chem.*, **13**, 1119 (1921).
[11] U.S. Pats. 1176378 (1916); 1230599 (1917); 1373661 (1921).
[12] U.S. Pat. 1231554 (1917).
[13] Bancroft, *J. Phys. Chem.*, **17**, 501 (1913).
[14] Briggs and Schmidt, *J. Phys. Chem.*, **19**, 484 (1915).
[15] Cf. Clayton, "Margarine" (1920), p. 71.
[16] *J. Phys. Chem.*, **18**, 45 (1914).

content of the latter.[1] Briggs and Schmidt [2] found that over 90 per cent. by volume of water can be emulsified in benzene, as in white lead paints containing rosin. They also investigated the emulsification of water in benzene, using Mg oleate as the emulsifier. By the gradual addition of water to benzene containing 1 per cent. Mg oleate, an emulsion so concentrated as to contain 90 per cent. water was obtained, of a stiff, jelly-like consistency (cf. Pickering's famous emulsion). This emulsion, however, would not remain stable for more than a few hours. Stiff, viscous emulsions of water in benzene were also prepared, using aluminium palmitate, but the water appeared as large irregular drops entangled in a voluminous precipitate of gelatinous nature. Such "quasi-emulsions" separated in about thirty minutes.

Finely-divided Solids as Emulsifiers.—Finely-divided solids in certain instances may promote emulsification of oils in water or of water in oil. Thus Tfol [3] found that a North African argillaceous earth readily emulsified oils in water, and could be used as a substitute for soap. The first extensive survey of insoluble emulsifiers, however, was made by Pickering,[4] who found that the basic sulphates of iron, copper, nickel, zinc and aluminium act as efficient emulsifying agents for dispersing mineral oil in water. Other useful emulsifiers were freshly-precipitated calcium carbonate and arsenate, lead arsenate, and various unheated fine clays. Unstable quasi-emulsions were promoted by lime, silica, dried alumina or plaster of Paris; also by freshly-precipitated basic cadmium sulphate, magnesium hydroxide, copper hydroxide, tin oxychloride, and the sulphides of iron and copper. Pickering [5] believed that emulsification depended on the size of the particles constituting the emulsifier, and that the size of the emulsion globules varied directly with the size of the particles of the emulsifying agent.[6] He also pointed out the perfectly correct

[1] Bancroft, *J. Phys. Chem.*, **17**, 514 (1913).
[2] *J. Phys. Chem.*, **19**, 491 (1915).
[3] *Pharm. J.*, **6**, 1228 (1898).
[4] *J. C. S.*, **91**, 2001 (1907).
[5] *J. S. C. I.*, **29**, 129 (1910).
[6] In this connection reference should be made to Jerome Alexander's interesting paper on "The Zone of Maximum Colloidality" (*J. Amer. Chem. Soc.*, **43**, 434 (1921)).

condition that for emulsions of oil in water the finely-divided solid emulsifying agent must be more readily wetted by water than by oil.

Briggs and Schmidt [1] found that hydrous ferric oxide in aqueous suspension is a "fairly good" emulsifier for benzene. Later Briggs [2] showed that hydrous ferric oxide, arsenious sulphide, and finely-powdered silica promote emulsions of benzene and kerosene in water. On the other hand, carbon black and mercuric iodide promote the emulsification of water in benzene or kerosene.

Schlaepfer [3] in 1918 formulated that "insoluble particles, which are more easily moistened by oil than by water, will have a tendency to facilitate the emulsification of water in oil." He found that 70 per cent. by volume of water could be dispersed in 30 per cent. by volume of kerosene, using 1 gram of carbon (best American soot), giving a very viscous emulsion, stable for at least a week. It was found impossible to obtain an emulsion of kerosene in water with the aid of carbon. These results were confirmed by Moore,[4] who studied the emulsification of water and of aqueous solutions of ammonium chloride in kerosene. He found (1) that, on the whole, the larger the amount of carbon (lamp-black) used, the smaller were the diameters of the emulsified water globules; (2) if the volume of kerosene be kept constant, the average diameters of the emulsified globules increase as the total volume of the liquids increases. The more concentrated emulsions, particularly with 50 per cent. by volume of normal $NH_4.Cl$ dispersed therein, were firm and stiff, of a buttery consistency, and very stable. To make 30 c.c. of such an emulsion required the presence of 0·5 gram of lamp-black.

Briggs [5] showed that certain finely-divided solids, when used together, could exert antagonistic emulsifying effects. For example, if to 0·8 gram of carbon black, normally capable of promoting the dispersion of 25 c.c. of water in 15 c.c. kerosene,

[1] *J. Phys. Chem.*, **19**, 484 (1915).
[2] *J. Ind. Eng. Chem.*, **13**, 1008 (1921).
[3] *J. C. S.*, **113**, 522 (1918).
[4] *J. Amer. Chem. Soc.*, **41**, 940 (1919).
[5] *J. Ind. Eng. Chem.*, **13**, 1008 (1921).

one added 0·1 gram of silica (350 mesh), no emulsion was possible. On the other hand, kerosene can be emulsified in a water suspension of silica, but if sufficient carbon black be present no emulsion can be made. Similarly, 1 part of mercuric iodide in 20 parts of silica will prevent the latter from emulsifying 25 c.c. of kerosene in 25 c.c. of water. So far no work has been done on the possible antagonistic effects of finely-divided solids and substances in colloidal solution, such as soaps or gelatin, though the results would have great theoretical significance.

Colloidal clay as an efficient emulsifying agent for oil and fats has been investigated by Weston.[1] According to him, however, colloidal clay is capable of facilitating the emulsification of oil in water or of water in oil.[2] Such a result certainly demands further investigation, as it is at present understood that a given emulsifying agent only promotes *one* type of emulsion with any two given liquids to be emulsified. Kieselguhr has been used by Lapworth and Pearson [3] as an emulsifying agent when studying the reduction of emulsified nitro-compounds. Sheppard [4] used salts of low solubility, *e.g.*, $PbSO_4$, for emulsifying nitrobenzene in mineral acids.

Bhatnagar [5] used such precipitates as zinc hydroxide, aluminium hydroxide and lead oxide for making emulsions of the water-in-oil type (see Chapter V.).

An extensive investigation on the use of finely-divided solids as emulsifiers has been carried out by Bechold, Dede, and Reiner.[6] They found that the formation of emulsions depends upon : (1) The grain size of the powder. The smaller the grain the better is the emulsion, until an optimum is reached, after which smaller grains have inferior emulsifying properties. (2) The quantity of powder. The more powder there is available the more globules there can be covered, providing the powder is sufficiently fine.

The solids investigated were zinc dust, iron powder, clay, kieselguhr and yeast, and they were found to be as efficient as

[1] *Chemical Age*, **4**, 604, 638 (1921).
[2] *Loc. cit.*, p. 640.
[3] *J. C. S.*, **119**, 765 (1921).
[4] *J. Phys. Chem.*, **23**, 634—9 (1919).
[5] *J. C. S.*, **119**, 1760 (1921).
[6] *Koll. Zeits.*, **28**, 6—19 (1921).

hæmoglobin or egg-albumin solutions for emulsifying benzene, paraffin oil, nitrobenzene, aniline, isobutylaldehyde, carbon disulphide, and several other organic liquids, in water.

The Efficiency of Emulsifying Agents.—No systematic attempt has been made to arrange all the various emulsifying agents in the order of their capacity to promote and maintain stable emulsions. Thus it is only known in a general kind of way that certain substances are better emulsifiers than others for emulsions of, for example, pure olive oil in water or a pure mineral oil in water.

Moore and Krumbholz [1] have published a note on "the relative power of various forms of proteid in conserving emulsions." Preparing olive-oil-in-water emulsions, they found the following proteids to possess emulsifying efficiencies in the ascending order: albumose, blood serum, white of egg, acid albumin, and alkali albumin. The albumose was practically ineffective, blood serum and white of egg were only poor emulsifiers, whilst the two albumins were very effective. The results obtained, however, were only of a qualitative nature.

Recently, Clark and Mann [2] have studied the emulsifying efficiencies of sucrose, dextrin, starch, gum arabic, and egg albumin. Emulsions of benzene and of kerosene were made in aqueous solutions of the emulsifying agents at various concentrations. In each instance the oil phase was 75 per cent. of the total volume. After seven weeks the emulsions were graded on a scale of ten as regards stability, *i.e.*, efficiency of the emulsifying agents.

Thus, using 1 per cent. solutions of the emulsifiers and dispersing benzene therein, the following gradation was given: egg albumin, 10; starch, 6; gum arabic, 5; dextrin, 3; sucrose, 0. When kerosene was emulsified, the gradation appeared as: egg albumin, 10; starch, 9; gum arabic, 3; dextrin, 2; sucrose, 2.

The presence of electrolytes influenced the emulsifying efficiencies, but egg albumin still stood out as the most effective

[1] *Proc. Physiol. Soc., London*, **54**, 22 (1898). Very similar observations have also been made by Fischer and Hooker, "Fats and Fatty Degeneration" (1917), p. 32.

[2] *J. Biol. Chem.* **52**, 160 (1922).

emulsifier, and the emulsions still received 10 points on the arbitrary scale, when HCl, NaI, NaOH, $NaHCO_3$, or Na_2SO_4 were present in the continuous phase.

Marshall [1] carried out some experiments on emulsifying power, and found that whilst 1 gram of gum acacia in 4 c.c. water will emulsify 21 c.c. of almond oil, 1 gram of soft soap in 4 c.c. water will emulsify 210 c.c. of almond oil. A solution of 0·2 gram of saponin in 4 c.c. of water could emulsify 90 c.c. of almond oil. Marshall then determined the quantities of various emulsifiers and water required to emulsify 200 c.c. of almond oil. The experiments were carried out at 13° C., the method employed being the pharmaceutical one of trituration in a mortar. The quantities required were: gum acacia, 10 grams in 23 c.c. water; soft soap, 1 gram in 3·8 c.c. water; saponin, 0·2 gram in 9·6 c.c. water; condensed milk, 5 grams in 20 c.c. water.

Crockett and Oesper,[2] and also Hiss,[3] have qualitatively found that gum tragacanth is much inferior to gum acacia for preparing pharmaceutical emulsions. Briggs and Schmidt [4] have mentioned that for emulsifying benzene in water 1 per cent. gum arabic solution is inferior to 1 per cent. gelatin solution, this in turn being much inferior to the alkali soaps.

Pickering [5] graded "good" emulsifiers of mineral oils in water as follows: Soft soap is the most effective. "Dissolved starch, milk and flour are good, though the latter forms a flocculent and not a creamy emulsion. Milk gives rise to solid clots. Glue emulsifies well and so does egg-albumin, but the emulsion with the latter is rather frothy owing to enclosed air bubbles. Saponia and quillaia bark give good emulsions when the proportion of oil present is not large."

The emulsifying efficiency of the sodium salts of the paraffin series of fatty acids have been studied by Donnan and Potts,[6] using a pure hydrocarbon oil and water. Only the higher

[1] *Pharm. J.*, **28**, 257—266 (1909).
[2] *J. Ind. Eng. Chem.*, **9**, 967 (1917).
[3] *Bull. Pharm.*, **13**, 229 (1899).
[4] *J. Phys. Chem.*, **19**, 484 (1915).
[5] *J. C. S.*, **91**, 2002 (1907).
[6] *Koll. Zeits.*, **7**, 208 (1910).

members of the series, from sodium laurate onwards, acted as emulsifying agents. Donnan and Potts connected this fact with the colloidal nature of the solutions of the higher soaps.[1]

Briggs and Schmidt [2] observed that sodium resinate (pure resin soap) was not so efficient as sodium oleate for emulsifying benzene in water. White and Marden[3] investigated the emulsifying capacities of sodium stearate and sodium palmitate for preparing emulsions of kerosene and linseed oil in water, correlating the results with the values for the surface tensions of the soap solutions. No very definite data on emulsifying efficiencies were obtained.

As regards emulsifiers for preparing water-in-oil emulsions, practically nothing has been done in the way of a quantitative arrangement of their emulsifying powers. Briggs and Schmidt found that Ba oleate is much less effective than Mg oleate for emulsifying water in benzene, whilst Mg resinate, Cu resinate, and Pb oleate were non-effective.

The emulsifying efficiency of finely-divided solids is a question of much difficulty. In a general way, Pickering found that the basic sulphate of iron is very effective for dispersing oils in water. Then, in descending order of efficiency, come the basic sulphates of copper, nickel and aluminium. Lime, silica, alumina, plaster of Paris, and fine powders which have been dried only promote unstable quasi-emulsions.

The chief points to be studied in any attempt to grade finely-divided solids as emulsifiers for a given oil and water will be : (1) the wetting of the solid by each of the liquids, as determined, for instance, by the measurement of contact angles ; [4] (2) the size of the particles ; (3) the amounts required under standard conditions.

The Emulsifiability of Oils in Water.—With a given emulsifying agent and water, it is theoretically possible that different oils will be capable of being emulsified to different extents. Very little quantitative work, however, has been carried out in

[1] See p. 49.
[2] *Loc. cit.*
[3] *J. Phys. Chem.*, **24**, 617 (1920).
[4] See p. 67.

this connection. Clayton [1] investigated the emulsifiability of certain edible oils and fats in water at various temperatures, using the Donnan drop-number method.[2] Very little difference indeed was found in the drop numbers of seven common oils and fats. Thus :—

Oil.	Temperature.	Drop Number.
	Deg. Cent.	
Arachis . .	25·5	66
	46·0	65
	50·0	64·5
Cottonseed . .	27·5	65
	35·0	65
	50·0	63
Coconut . .	30·0	69
	35·0	61
	50·0	65
Palm kernel . .	30·0	73
	35·0	74
	50·0	61
Lard . . .	35·0	59
	50·0	66
Oleo . . .	35·0	66
	50·0	69
Soya bean . .	35·0	68
	50·0	68·5

Meunier and Maury [3] investigated the emulsifiability of several oils in water by the drop-number method. The following figures were obtained at 21° C. :—

Neat's-foot oil	= 18 drops.
Olive oil	= 20 ,,
Linseed oil	= 18 ,,
Castor oil	= 9 ,,
Mineral oil (D = 0·934) . .	= 9 ,,

The first three oils are thus about twice as easily emulsified in

[1] *Trans. Farad. Soc.*, **16**, Appendix, p. 24 (1921).
[2] See p. 101.
[3] Collegium (1910), pp. 277—284, 285—287.

water than is castor oil or mineral oil. They found that temperature had practically no influence on the drop number, a result confirmed by Clayton's experiments.

The modern view of emulsions, considered from the Langmuir-Harkins theory of orientation,[1] is that oils and fats of animal or vegetable nature, being mixed glycerides, should have similar emulsifiabilities in water or soap solutions. Mineral oils should be less readily emulsified in water, since they do not possess carboxylic or other groupings with an affinity for water. In any case, the question of emulsifiability in water only is of minor importance, and is only investigated as a necessary preliminary to further work on emulsification in water containing emulsifying agents, these being necessary for all emulsions other than very dilute. Engineers, however, have been concerned with the question of the emulsification of the oil in forced-feed lubrication, and various tests have been devised to ascertain the extent to which a given lubricating oil will emulsify in water. Thus Herschel's [2] test is as follows : " One part of oil to two parts of water are stirred for five minutes in an ordinary 100 c.c. graduated cylinder at a specified speed and temperature by means of a flat, metal paddle. The emulsion thus formed is allowed to stand at the same temperature, and readings are taken at intervals of the volume of oil separated out. The maximum rate of settling, ascertained from a table, is called the ' demulsibility,' and is used as a measure of the resistance of the oil to emulsification."

The " demulsibility " of lubricating oils for use in steam turbines has also been studied by Philip,[3] Delbridge,[4] and Conradson.[5] No really satisfactory standard has been devised suitable for all classes of lubricating oils.

Leaving the question of the emulsifiability of oils in water, and considering water containing an emulsifying agent, the only investigation made has been on the emulsification of vegetable oils in soap solutions.

[1] See p. 69.
[2] *Proc. Amer. Soc. Testing Materials*, **16** (part 2), 248—265 (1916); also *U.S. Bur. Standards, Tech. Papers*, No. **86**, pp. 1—37 (1917).
[3] *J. S. C. I.*, **34**, 697 (1915).
[4] *Proc. Amer. Soc. Testing Materials*, **20** (part 1), 416—426 (1920).
[5] *Ibid.*, **16** (part 2), 273—280 (1916).

Lehner and Bishop [1] determined the emulsifiability of eight oils in sodium oleate solutions at 100° C. Plotting their results with " per cent. by volume of oil emulsified " as ordinates, and the " minimum amount of sodium oleate " emulsifier required as abscissæ, closely similar curves were obtained with cotton-seed, maize, linseed, olive, rape, arachis, sesame and castor oils, showing that they were all emulsified to about the same extent.

[1] *J. Phys. Chem.*, **22**, 68 (1918).

CHAPTER II

THE PROPERTIES OF EMULSIONS

WITHOUT the presence of an emulsifying agent, emulsions of oil in water may be made up to a maximum concentration of 2 per cent.[1] Usually, however, pure oil-in-water emulsions are very dilute, the oil content being of the order of 1 in 10,000. Apart from condensed water in engineering practice, such emulsions are of little or no significance technically. They have a very important bearing, however, on the theoretical side, owing to their great similarity to colloidal suspensions, and because several interesting facts have been established for which no satisfactory explanation is yet available.

In the first place, with pure oil and pure water only, but one type of emulsion is known, viz., that in which the oil is dispersed in water. Groschuff [2] claimed to have prepared very dilute emulsions of water in benzene and mineral oils by heating the water and oil in a sealed vessel and then cooling down to 18° C. The emulsion in benzene was stable for a few minutes, that in petroleum for one hour, whilst paraffin oil, and particularly transformer oil, gave stable emulsions. Very similar results have been published by Hall.[3] The noteworthy feature in the results of both these workers is that the purer the materials, the less stable were the emulsions. The more stable emulsions were in each case in oils where colloidal matter is in all probability present. Consequently, with pure oil and water we only know stable emulsions of the oil-in-water type. No observer has ventured an explanation for this fact, and an excellent line of research is open for an investigation on the possibility of making water-in-oil emulsions, using materials beyond suspicion.

[1] Lewis, *Koll. Zeits.*, **4**, 211 (1909).
[2] *Koll. Zeits.*, **9**, 257—9 (1911).
[3] *J. Phys. Chem.*, **21**, 609 (1917).

The Size of Particles.—The oil globules in pure oil-in-water emulsions have diameters of the order of 10^{-5} cm., as compared with 10^{-3} cm. for colloidal suspensions. Donnan,[1] investigating the stability of colloidal solutions and emulsions in relation to surface tension, on thermodynamical considerations, predicted a critical diameter of particle when one phase is very finely divided in the other. The order of magnitude expected is 10^{-5} cm.

Lewis [2] demonstrated in approximate manner the existence of this critical or equilibrium size of globule in the case of several emulsions of oil in water. By shaking a purified mineral oil in water for forty-eight hours he obtained an emulsion (whose maximum oil content was 2 per cent.) in which the oil globules had a diameter of 4×10^{-5} cm., a value of the same order as found by Burton [3] for colloidal metals. Lewis now prepared emulsions by (*a*) boiling oil and water together under a reflux condenser for thirty hours, producing partial emulsification; (*b*) pouring an alcoholic solution of oil into water, producing a milky emulsion; and (*c*) steam-distilling aniline, forming an unstable emulsion of aniline in water. In all cases the drops possessed diameters of the order of 10^{-5} cm.

Lewis [4] has discussed the limiting size of emulsion globules in relation to interfacial tension and electric charge. Assuming the globules are isolated, charged spheres, the charge being independent of the size, the opposing effects of interfacial tension and electric charge can be equated and the relation deduced that

$$r = \sqrt[3]{\frac{e^2}{16\pi\sigma K}},$$

where r is the radius of a globule, e the electric charge, K the dielectric constant, and σ the interfacial tension between the oil and water. When this equilibrium is realised, the effect of curvature on solubility ceases, and the globules can remain in equilibrium with a plane surface. Knapp [5] has extended

[1] *Zeits. phys. Chem.*, **46**, 197 (1903); cf. also *ibid.*, **37**, 735 (1901).
[2] *Koll. Zeits.*, **4**, 211 (1909).
[3] *Phil. Mag.*, **11**, 425; **12**, 472 (1906).
[4] *Koll. Zeits.*, **5**, 91—3 (1909).
[5] *Trans. Farad. Soc.*, **17**, 457—465 (1922).

these considerations and shown that, if S_r be the solubility of a colloid particle of radius r, and S the usual or normal solubility, then

$$S_r = S_\epsilon^{\frac{\alpha}{r} - \frac{\beta}{r^4}} \quad . \quad . \quad . \quad . \quad . \quad (I.)$$

when α and β are constants and equal to $\frac{2\sigma M}{RTd}$ and $\frac{e^2 M}{8\pi K R T d}$ respectively, where M = the molecular weight of the dispersed phase, R the gas constant, T the absolute temperature, and d the density of the dispersed phase.

By differentiation,

$$\frac{dS_r}{dr} = S_\epsilon^{\frac{\alpha}{r} - \frac{\beta}{r^4}} \left(\frac{4\beta}{r^5} - \frac{\alpha}{r^2} \right) \quad . \quad . \quad . \quad (II.)$$

which is equal to zero when

$$r = \sqrt{\frac{4\beta}{\alpha}} = \sqrt[3]{\frac{e^2}{4\pi K \sigma}} \quad . \quad . \quad . \quad (III.)$$

When r has this value, the second differential of (II.) becomes negative, so that there is a maximum solubility at this point. When r approaches zero, S_r approaches zero; when r is infinite, S_r is equal to S. These results are expressed by Knapp as a graph in Fig. 1.

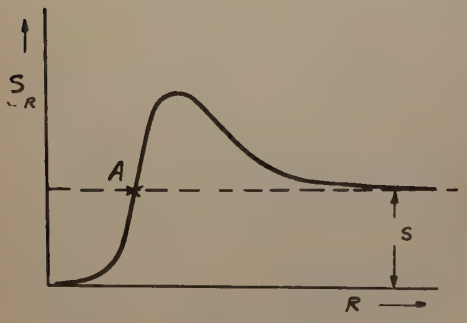


Fig. 1.

In making emulsions the dispersed phase is present both as large masses and small globules. The drops increase or decrease in size until their solubility becomes the same as that of the mass in bulk, which possesses an approximately plane surface.

For a particle with a finite radius to be in equilibrium with a flat surface the solubility must be equal to S. From equation (I.) this value for S_r is given when

$$\epsilon^{\frac{\alpha}{r} - \frac{\beta}{r^4}} = 1,$$

that is, when $$\frac{\alpha}{r} - \frac{\beta}{r^4} = 0,$$

or $$r = \sqrt[3]{\frac{\beta}{\alpha}} = \sqrt[3]{\frac{e^2}{16\pi K\sigma}}.$$

This equilibrium value of the radius is shown in the graph as the ordinate of the point A.

For the further mathematical treatment of the subject, especially in relation to the question of electrical double-layer effects, Knapp's paper should be consulted.

Whilst Lewis found 10^{-5} cm. to be the order of the diameters of his emulsion particles, Ellis,[1] using very similar emulsions, prepared by shaking a special acid-free cylinder oil with water for two or three days, obtained globules of the order 2×10^{-4} cm. Electrolytes had marked effects on the size of the globules, as we shall see later. Powis,[2] for similar emulsions, found that few globules exceed 3×10^{-4} cm., or were less than $0{\cdot}5 \times 10^{-4}$ cm.

It is of interest now to mention the globule sizes of some typical three-phase emulsions for the purpose of comparison. Baldwin [3] found that the butter-fat globules in cow's milk were from 0·005 to 0·006 mm. diameter (5 to 6 μ). By homogenising —*i.e.*, further subdividing—the globules (see Chapter VIII.) the diameters were reduced to 1 or 2 μ. Schultz and Chandler [4] have found that, whilst in cow's milk 90 per cent. of the globules exceed 4 μ, in goat's milk 91 per cent. of the globules are less than 4 μ, and of these over 50 per cent. are less than 2 μ. Bechold [5] examined cow's milk, and found the diameters of the globules to average 3 μ, but the actual range of the particles was from 0·1 μ to 22 μ.

Rubber latex emulsion examined by Henri [6] contained particles approximately 50 per cent. of which had diameters of 2 μ, the remainder being 0·5 μ in diameter. Roon and

[1] *Zeits. phys. Chem.*, **80**, 604 (1912).
[2] *Ibid.*, **89**, 91 (1915).
[3] *Amer. J. Pub. Health*, **6**, 862 (1916).
[4] *Jour. Biol. Chem.*, **46**, 133 (1921).
[5] "Colloids in Biology and Medicine" (1918), p. 346.
[6] *Koll. Zeits.*, **1**, 116 (1906); cf. Fickendey, *ibid.*, **8**, 43—7 (1911); Geer, *J. Ind. Eng. Chem.* **14**. 370 (1922).

Oesper [1] made emulsions of cotton seed oil, benzene, paraffin, carbon tetrachloride and chloroform in dilute soap solutions. The globules were about 1 or 2 μ in diameter. If gum acacia solutions were used instead of soap solutions, larger globules resulted, the diameters being from 3 to 50 μ.

The Concentration of Emulsions.—It has already been remarked that, for pure oil and water, 2 per cent. of oil is the maximum amount that has so far been emulsified in water. Theoretically, if the oil globules be considered as rigid spheres of equal diameter, it should be possible to pack them together in such a way that each sphere will touch twelve others. This maximum packing—*i.e.*, concentration—occurs when about 74 per cent. of the total available space is occupied by the spheres. Hence approximately 74 per cent. of oil can theoretically be dispersed in about 26 per cent. of water.[1] For deformable spheres, such as the oil globules really are,[2] flattening of the spheres can occur at the points of contact, and polyhedral forms ensue. In fact, experiments have shown that stable emulsions containing even 99 per cent. of the disperse phase may be obtained.[3]

Such concentrated emulsions, however, demand the presence of a third substance, capable of forming an adsorbed film at the oil/water boundary. The theoretical case of 74 per cent. pure oil being dispersed in 26 per cent. pure water has never been realised, and neither has the reverse case. The 2 per cent. limit obtained by Lewis is bound up with the whole vexed question of saturation-concentration in colloidal systems generally. At the present time our knowledge of the actual mechanism of colloidal solubility, whether for emulsions, suspensions, or so-called colloidal solutions, is insufficient to account for the fact that, in general, pure two-phase systems only seem to be stable over low concentration ranges.[4]

The Electric Charge.—The oil globules in emulsions of oil in water carry a negative charge, as proved by cataphoresis tests.

[1] See p. 31.
[2] Cf. Hatschek, *Koll. Zeits.*, **7**, 81 (1910).
[3] Pickering, *Koll. Zeits.*, **7**, 11 (1910).
[4] For a fuller discussion on saturation in colloid solutions, see Ostwald, "Handbook of Colloid Chemistry" (1919), pp. 132—45.

The origin of this charge is still open to question, as is, indeed, the more general case of the electric charge of all colloid particles. For a time an empirical rule due to Coehn[1] was accepted, viz., that for two phases in contact, the phase with the higher dielectric constant assumes the positive charge. Apart from the fact that no clue is given as to the origin of this charge, many exceptions to the rule are now established.

The electric charge is now believed to be due to the adsorption of ions. In the case of emulsions bearing a negative charge, adsorption of OH' ions at the surface of the oil globules is postulated. Even when emulsions are made with absolutely pure oil and pure water there must be present hydrogen and hydroxyl ions due to the ionisation of the water, and consequently adsorption of OH' ions can take place. No definite idea of the actual mechanism of such adsorption, however, is available, though in this connection Mukherjee[2] has published an important paper dealing with the nature of the chemical forces to which adsorption may be due.

The adsorbed ions are considered to be concentrated near the surface of the globules, in the layer of the liquid immediately bathing the globules. An equivalent amount of ions of opposite sign is necessarily postulated as being present in the liquid. The distance between a globule and its adsorbed "layer" of ions is estimated[3] to be about 5×10^{-7} cm. The ions imparting the charge to the surface are situated wide apart from each other compared to molecular dimensions.

The two layers of oppositely-charged ions are frequently referred to as the *Helmholtz double layer*.[4] The oil globule and its double layer may be considered as a small condenser, a definite potential difference existing between the oil and the nearer ionic layer. Such a system should be self-contained and electrically neutral to an external field, and for this reason a certain "give" or "facility of slip" is postulated between

[1] *Wied. Ann.*, **64**, 227 (1898); *Zeits. Elektrochem.*, **16**, 586 (1910).
[2] *Trans. Farad. Soc.*, **16**, Appendix, 103—115 (1922).
[3] von Hevesy, *Koll. Zeits.*, **21**, 129 (1917).
[4] *Wied. Ann.*, **7**, 337 (1879).

the nucleus and the outer ionic layer,[1] since the oil globules in emulsions wander to the anode in an electric field.

Lewis [2] determined the P.D. (potential difference) between the oil globules and water in a purified mineral oil emulsion. A cataphoresis test in a U-tube at 25° C. under the application of an E.M.F. of 230 volts showed that the oil globules wandered at the rate of $4{\cdot}3 \times 10^{-4}$ cm. per second for a potential gradient of 1 volt per cm. Employing Burton's [3] expression,

$$V = \frac{4\pi\eta v}{KX},$$

where V = P.D. between an oil globule and the water,
K = the dielectric constant of the water,
η = the viscosity of the water,
v = velocity of the globule in cm. per second under an applied potential gradient of X volts per cm.,

the value of V was found to be 0·05 volt. Lewis [4] later obtained the value of V for a hydrocarbon oil emulsion as 0·060 volt. Ellis [5] determined, by careful cataphoresis experiments, the following values for the mobilities of the oil globules in dilute two-phase emulsions, and for the P.D. between the oil and the water :—

Oil.	*Mobility* in cm./sec., per volt/cm. $\times 10^{-4}$.	*P.D.* in volts.
Special acid-free oil	3·59	0·050
Acid-free oil	3·24	0·045
Pure liquid paraffin	2·93	0·040
Cylinder oil	2·70	0·050
Water-soluble oil	4·80	0·066
Aniline (freshly distilled)	—	0·043
Chloroform	1·00	0·014
Gummigutt	1·81	0·025
Mastixharz	1·77	0·024

[1] Lamb, *Phil. Mag.* (1888).
[2] *Koll. Zeits.*, 4, 211 (1909).
[3] *Vide* "Physical Properties of Colloidal Solutions," 2nd ed. (1921), p. 137.
[4] *Phil. Mag.*, 19, 573 (1910).
[5] *Zeits. phys. Chem.*, 78, 321 (1912).

The electric charge carried by the oil globules must now be considered. The *absolute* charge is not measured, but rather the *effective* charge, which has a smaller value, depending upon the "give" of the electric double layer. Considering the emulsion globule in water as a colloid-condenser system, it is obvious that if there is no "give" or "facility of slip" the effective charge would be zero, although the real charge might be considerable.

Burton[1] has developed the Helmholtz-Lamb theory dealing with the charges carried by colloids. Lamb's expression for the velocity (v) of a charged particle through a liquid under an electric force, when the motion has become steady, is

$$Xe = 4\pi a^2 \eta v \frac{1}{l} \quad . \quad . \quad . \quad . \quad \text{(I.)}$$

where X = gradient of electric potential in the liquid,
e = charge on the particle,
a = radius of the particle,
η = coefficient of viscosity of the liquid,
l = a linear magnitude measuring the facility of slipping. This is equal to η/β, where β is the coefficient of sliding friction of the fluid in contact with the wall of the tube.

Considering the particle with its electrical double layer as a small condenser of two concentric spheres, whose distance apart (d) is small compared with (a), it follows that the capacity (C) of this condenser will be

$$C = \frac{a^2}{d} K \quad . \quad . \quad . \quad . \quad \text{(II.)}$$

where K is the specific inductive capacity of the liquid. If V indicates the contact difference of potential between the solid and the liquid, we have (since $Q = eV$)

$$e = V \frac{a^2}{d} K \quad . \quad . \quad . \quad . \quad \text{(III.)}$$

[1] *Phil. Mag*, **11**, 425; **12**, 472 (1906); *Brit. Assoc. Colloid Reports*, **4** (1922), p. 23.

Substituting this value of e in equation (I.), and transposing, we get

$$V\frac{l}{d} = \frac{4\pi}{K} \cdot \frac{\eta v}{X} \quad . \quad . \quad . \quad . \quad . \quad (IV.)$$

All electric measurements are expressed in electrostatic units. Lamb has given reasons for believing l and d are of the same order of magnitude (10^{-8} cm.), and Burton therefore regards $\frac{l}{d}$ as approximately unity, whereupon

$$V = \frac{4\pi}{K} \cdot \frac{\eta v}{X} \quad . \quad . \quad . \quad . \quad . \quad (V.).$$

This expression we have already noted as being employed by Lewis for determining the P.D. at the oil-globule/water boundary.

Using equation (III.), Lewis [1] calculates the charge (e) on the particles in his oil emulsion to be 4×10^{-4} electrostatic units. Similarly, using data by Burton for colloidal solutions of silver and platinum, Lewis finds the charge on the particles to be 8×10^{-5} electrostatic units.

In the use of these formulæ, to yield exact results, it should be remembered that the values of d and l are still in doubt. If l/d is not unity after all, the values of V will be wrong. Again, as Burton points out, it is a question of what value to assign to K, since it applies to the medium separating the positive and negative Helmholtz layers.

Brownian Movement in Emulsions.—Suspensions of fine particles, fine-grained emulsions, and colloidal solutions of metals, hydroxides and sulphides all show, when examined under the ultramicroscope, that the particles of the dispersed phase are in continuous zigzag motion. The phenomenon is termed the Brownian motion, after Brown,[2] who studied the movements of pollen grains in water. It is now agreed that the movements of finely-divided particles suspended in liquids is due to the bombardment of the particles by the molecules of the surrounding liquid.

The Brownian motion does not begin in suspensions until

[1] "System of Physical Chemistry," Vol. I. (2nd ed.), p. 334.
[2] *Phil. Mag.*, 4, 161 (1828); 6, 161 (1829).

the diameters of the particles are reduced to below 3 to 5 μ.[1] As the particles decrease in size under constant conditions the Brownian movements become more rapid, and translatory or progressive motion is apparent. Exner [2] examined gutta-percha emulsions at 23° C., and obtained the following figures for the dependence of the Brownian motion on the size of particles :—

Diameter of Particles.	Velocity of Particles.
1·3 μ	2·7 μ per second.
0·9 μ	3·3 μ ,,
0·4 μ	3·8 μ ,,

For a gamboge suspension he found that a variation in the diameter from 0·4 μ to 1·3 μ altered the velocity from 3·8 μ to 2·7 μ per second. At 3 μ the motion was hardly perceptible, whilst at 4 μ it was *nil*.

The Brownian movement has been the subject of numerous investigations,[3] and has played a most important part in proving the real existence of molecules.[4] In the present volume, however, it is only mentioned as a property of emulsions. Whenever emulsions are treated so that the globules coalesce to particles whose diameters exceed 4 μ, the Brownian motion ceases. Thus Henri [5] found (using the cinematograph) that, when a rubber emulsion is treated with acetic acid, the motion slows down before coagulation actually occurs, whereupon it ceases altogether. In general, Brownian motion is believed to cease when the iso-electric (electrically neutral) point is reached.

The Stability of Emulsions.—We have already noted that concentrated emulsions demand the presence of an emulsifying agent. In such cases the stability of the emulsion depends on factors chiefly relating to an adsorbed film at the oil/water boundary. This subject is discussed later (Chapter V.).

For emulsions of oil in pure water the stability is influenced by (*a*) the interfacial tension, tending to bring about coalescence

[1] Wiener, *Pogg. Ann.*, **118**, 79 (1863).
[2] *Ann. Physik.*, **2**, 843 (1900).
[3] See the excellent account in Burton's "Physical Properties of Colloidal Solutions" (1921), Chap. 4.
[4] Perrin, *Koll. Beihefte*, I. (1906).
[5] *Bull. Soc. Fr. Phys.* **4**, 45, 61 (1908).

of the globules, whereby the total surface would be reduced; (*b*) the Brownian movement, tending to collision of the globules, a factor against stability; and (*c*) the electric charge on the globules, tending to repel them on near approach.

For two-phase emulsions, such as were studied by Lewis,[1] Ellis, Powis and Hatschek, the interfacial tension between the oil and water is of the order of 48 dynes/cm. Pockels [2] found the value 48·3 dynes/cm. for the interfacial tension between water and a petroleum oil.

Most of the work on emulsion stability relates to the influence of added electrolytes. Hardy [3] suggested that, when colloid particles are coagulated under the influence of electrolytes, the globules adsorb oppositely-charged ions, so that their charges become neutralised, and at the iso-electric point, where the potential difference between the particles and the medium becomes zero, stability is least. Coagulation occurs over a *range* whose magnitude depends on the extent of the coagulating factors. Bredig [4] correlated Hardy's view with the Lippmann effect (connecting surface tension and potential difference), and proposed a theory of colloid coagulation as follows. The interfacial tension between colloid particles and their medium acts in such a way that any increase in this tension tends to bring about a decrease in the surface exposed, *i.e.*, by coagulation of the particles. Now the interfacial tension between mercury and an electrolytic solution is a maximum when the P.D. between the two phases is zero. Hence, if the P.D. between colloid particles and their medium be decreased, as by the adsorption of oppositely-charged ions from added electrolytes, the stability is weakened by the resulting coalescence.

Ellis,[5] however, showed that Bredig's theory does not hold in the case of pure oil-water emulsions. He found his emulsions most stable in the presence of 0·001 normal NaOH, at which concentration the contact potential was a maximum. Ellis

[1] Lewis, *Phil. Mag.* (1908), p. 509.
[2] *Wied. Ann.*, **67**, 668 (1899).
[3] *J. Physiol.* **24**, 288—304 (1899); *Zeits. phys. Chem.* **33**, 385—400 (1900); *Nature*, **109**, 226 (1921).
[4] "Anorganische Fermente" (Leipzig), 1901.
[5] *Trans. Farad. Soc.*, **9**, 14 (1913).

found that the rate of coagulation of the oil globules was practically independent of the interfacial tension, depending only on the electric potential at the surface of the globules. On adding HCl to an oil-in-water emulsion the interfacial tension did not vary within the limits of experimental error, whilst the stability decreased enormously as the acid was added. Ellis collected his data *re* the effect of acid and alkali on the interfacial tension, the interfacial P.D., and the radius of the globules, in the graph reproduced in Fig. 2.

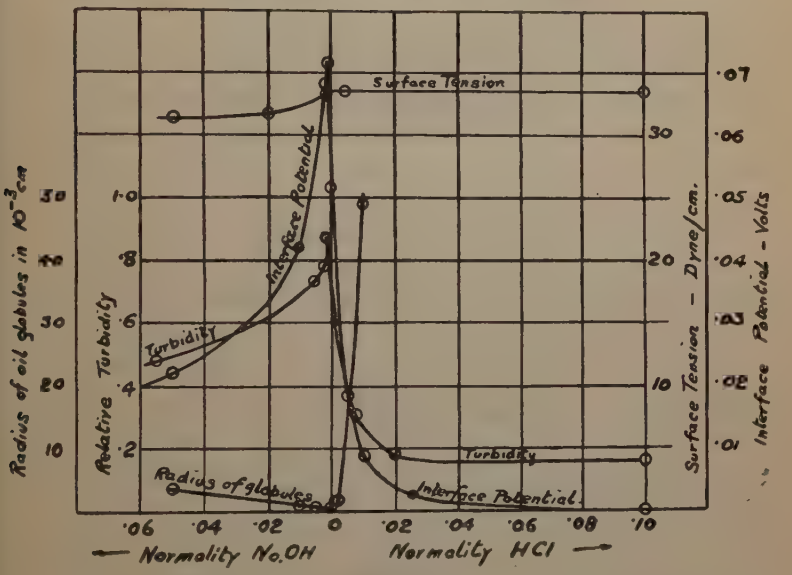


FIG. 2.

Powis [1] studied the effect of KCl, $BaCl_2$, $AlCl_3$, and $ThCl_4$ on the P.D. at the interface between oil and water in emulsions of cylinder oil in water. For the pure emulsion the P.D. was 0·046 volt, the sign being negative. When KCl was added the negative potential was raised at first, but with greater amounts of KCl it was depressed. A similar maximum was found by Ellis for NaOH. If $BaCl_2$ be added to the pure emulsion the P.D. is altered in sign, assuming a small positive value. With $AlCl_3$ the P.D. becomes positive, and then remains constant,

[1] *Zeits. phys. Chem.*, **89**, 91 (1914).

whilst with $ThCl_4$ the P.D. becomes positive, passing through a maximum and then decreasing, still retaining the positive sign.

The capacity of the four chlorides to reduce the negative P.D. increases as the valency of the cation increases. Expressed in millimols per litre, the concentrations necessary to reduce the oil-water potential to *nil* (*i.e.*, to arrive at the iso-electric point) are found by Powis to be for one of the emulsions examined :—

KCl . . .	about 5,000
$BaCl_2$	95
$AlCl_3$	0·51
$ThCl_4$	0·0156

His results show that all anions strive to make the P.D. more negative, and all cations to make it more positive. Powis correlates his results with the views of Freundlich,[1] who believes that the effect of added electrolyte on the P.D. at the surface of a particle is due to the preferential adsorption of anions or cations. If the cation is more strongly adsorbed, the value of the P.D. falls; in the opposite case it rises.

Later, Powis[2] carried out measurements on oil-water emulsions to which small amounts of the four chlorides were again added. He obtained the very important result that, when the oil/water potential difference reaches a definite critical value of approximately 0·030 volt (+ or —) the emulsion is relatively stable. Should the P.D. be smaller, coagulation follows, with a velocity which is approximately the same for all values of the P.D. This behaviour contradicts the previously accepted view that the stability decreases continuously with the P.D. and that at the zero point (iso-electric point) coagulation occurs. Similar results were obtained by Powis,[3] using colloidal arsenic sulphide.[4] At present there is no satisfactory explanation for the existence of a critical P.D., and if further work shows the phenomenon to be general, Hardy's view must be considerably revised.

The work of Donnan's pupils, Ellis, Powis, Lewis and

[1] *Zeits. phys. Chem.*, **73**, 385 (1910).
[2] *Ibid.*, **89**, 186 (1914).
[3] *J. C. S.*, **109**, 734 (1916).
[4] Cf. Willows, *Trans. Farad. Soc.*, **16**, Appendix, p. 101 (1922).

Bhatnagar, on neutral oil emulsions shows that there is a close similarity between such "mechanical" emulsions and colloidal suspensions. In each the particles carry an electric charge of the same order of magnitude, the limiting grain-size is similar, the potential difference values are similar, and the conditions for stability under the action of adsorbed ions are also similar. Thus the electrical factors far outweigh the effect of interfacial tension.

Ellis [1] has emphasised the subject in his paper on "A Neutral Oil Emulsion as a Model of a Suspension Colloid," which recapitulates much of his previous work.

Bhatnagar [2] has made the comparison still more close in his work on the effect of dilution in relation to emulsion treatment with electrolytes. In his latest paper [3] results are given for the effects of KCl, $BaCl_2$, and $Al_2(SO_4)_3$ on emulsions twice, three times, and four times diluted. Using stable emulsions of pure aniline in water (concentration 0·847 gram per litre) at 46° C., where gravity influences are eliminated owing to the equal densities of the two liquids, he obtained the following results :—

Electrolyte Added.		Time for Perceptible Change in Emulsion.							
(gram. equivs./litre).		Emulsion.		Twice diluted.		Three times diluted		Four times diluted.	
		mins.	secs.	mins.	secs.	mins.	secs.	mins.	secs.
KCl	(*a*) 0·1	41	0	56	1	115	5	133	10
	(*b*) 0·139	12	8	20	5	41	0	63	9
$BaCl_2$	(*a*) 0·029	10	0	18	7	27	5	40	0
	(*b*) 0·040	2	0	4	6	7	0	13	2
$Al_2(SO_4)_3$	(*a*) 0·002	10	0	11	1	13	5	15	9
	(*b*) 0·005	2	0	2	53	3	58	7	2

[1] *Trans. Farad. Soc.*, **9**, 14 (1913).
[2] *Ibid.*, **16**, Appendix, p. 27 (1921).
[3] *Jour. Phys. Chem.*, **25**, 735—41 (1921).

Bhatnagar's results agree with the work of Westgren and Reitstotter [1] and Mukherjee [2] on the effect of dilution on the rate of coagulation of suspensoids. He also found that the order of the coagulating efficiency of electrolytes is given by

$$Al > Cr > Ba > Sr > K > Na.$$

This order agrees with the precipitating effect of electrolytes on such suspensoid systems as gold,[3] platinum,[4] copper ferrocyanide,[5] prussian blue,[6] and silver.[7]

The Viscosity of Emulsions.—The position regarding the viscosity of emulsions from a *quantitative* point of view is far from satisfactory, very little work having been done in this connection. Dilute two-phase emulsions show a viscosity not much greater than that of water. Viscosity increases rapidly as the volume of the dispersed phase increases, but in this case, of course, there arises the new factor of the presence of the emulsifying agent.

Hatschek,[8] assuming that the dispersed phase of an emulsion occupies at least 50 per cent. of the total volume, has deduced a formula for the viscosity of an emulsion, viz. :—

$$\eta = \frac{\sqrt[3]{A}}{\sqrt[3]{A} - 1},$$

where η = coefficient of viscosity of the emulsion.

$$A = \text{ratio, } \frac{\text{Total volume of emulsion}}{\text{Volume of dispersed phase}}.$$

The expression may be transformed thus :—

$$A = \left(\frac{\eta}{\eta - 1}\right)^3.$$

Hatschek prepared an emulsion of ordinary lamp paraffin oil in 0·75 per cent. soap solution, obtaining a fairly coarse emulsion containing even macroscopic oil globules. The relative viscosi-

[1] *Zeits. phys. Chem.*, **92**, 750 (1918).
[2] *J. C. S.*, **117**, 1569 (1920); cf. *J. C. S.*, **115**, 464 (1919).
[3] Galecki, *Zeits. anorg. Chem.*, **74**, 174 (1912).
[4] Freundlich, "Kapillarchemie" (1909), p. 352.
[5] Pappadà, *Koll. Zeits.*, **6**, 83 (1910).
[6] *Ibid.*, *Koll. Zeits.*, **9**, 136 (1911).
[7] *Ibid.*, *Gazz. Chim.*, **42**, 263 (1912).
[8] *Koll. Zeits.*, **7**, 301 (1910); **8**, 34 (1911); *Trans. Farad. Soc.*, **9**, 80—91 (1913).

ties of the soap solution (continuous phase) and the emulsion were 135·8 : 1609.

Assuming the viscosity of the continuous phase as unity, the viscosity (η) of the emulsion will be 11·85. Since A equals $\left(\frac{\eta}{\eta - 1}\right)^3$, it follows that A = 1·302. Thus the volume per cent. of the dispersed phase is as 100 : 1·302, *i.e.*, 76·7 per cent.

By "breaking" 50 c.c. of the emulsion with HCl, it was found that 39·9 c.c. of oil separated out, *i.e.*, the oil occupied 79·8 per cent. of the total volume, a result agreeing satisfactorily with the previous calculated value.

The viscosity of concentrated emulsions is intimately connected with the presence of adsorbed films around the dispersed globules. This is particularly manifested in the homogenisation of emulsions, *i.e.*, the increased dispersion of the internal phase, whereby the presence of adsorbed emulsifying agent at the greatly magnified interface confers a marked increase of viscosity to the system.[1]

Interesting work could be done in investigating the viscosities of emulsions identical in oil and water content but stabilised by different agents, *e.g.*, gelatin and a finely-divided solid, respectively. Also there remains the interesting case of retaining the same oil and water content, but emulsified into systems of the opposite phase type. If ever a satisfactory instance is forthcoming of a reagent being capable either of promoting the oil-in-water or the water-in-oil type of emulsion, the question of the relation of the phase type to viscosity would provide a field for investigation. An obvious extension of this work, as yet untouched, lies in the question of the plasticity of *solid* emulsions like margarine, where the oil phase may be internal or external, depending on the mode of production.

The Colour of Emulsions.—Emulsions of the oil-in-water type are usually white or pale yellow in colour. Very dilute emulsions, such as those prepared by Lewis, are practically clear in transmitted light, but show a bluish tinge in reflected light. The more concentrated the oil phase, the more pronounced becomes the white or creamy colour. Some emulsions

[1] *Vide* Wiegner, *Koll. Zeits.*, **15**, 105—123 (1914).

are coloured owing to the presence of a colouring substance in the oil, *e.g.*, butter, which contains carotin and xanthophyll pigments. Margarine is coloured artificially, certain oil-soluble azo-dyes being used for this purpose.

Emulsions with structural colours—so-called "chromatic emulsions"—have been prepared by Bodroux,[1] and by Holmes and Cameron.[2] These investigators showed that if emulsions be made of two liquids of equal refractive indices (ensuring transparency), but widely different optical dispersive powers (n_F—n_C), the system is comparable to a multitude of lenses or prisms, with consequent prismatic colour effects.

The continuous phase of the emulsion must contain two completely miscible liquids, one of them of high refractive index and high optical dispersive power. Gradually adding this mixture to a milky emulsion already at hand makes it possible to change gradually the refractive index and optical dispersive power of the emulsion, thus producing the chromatic range of colours. Holmes and Cameron prepared several emulsions exhibiting such colour effects, *e.g.*, potassium iodide in water has a high optical dispersive power and high refractive index; if a solution of K I be added to an emulsion of "Nujol" in sodium oleate solution, prismatic colours are secured. Change in temperature causes change in colours, owing to the unequal temperature effect on the optical dispersive powers of the phases.

Transparent emulsions are possible when the two liquids have the same values for the refractive index and optical dispersive power. Thus glycerol gives transparent emulsions in a solution of calcium oleate in carbon tetrachloride. Transparent emulsions of glycerol are also possible in liquid paraffin containing 2 per cent. of crêpe rubber as the emulsifying agent.

The production of transparent emulsions has been made the subject of a patent by Rector,[3] who proposes to make medicinal emulsions (*e.g.*, of cod-liver oil) transparent by bringing the refractive indices of the phases into closer similarity through the addition of salt or sugar.

[1] *Comptes rend.*, **156**, 772 (1913).
[2] *J. Am. Chem. Soc.*, **44**, 71—74 (1922).
[3] U.S. Pat. 1389161 (1921); *vide* also *Chem. Age* (N.Y.), **29**, 408 (1921).

CHAPTER III

EARLIER THEORIES OF EMULSIONS

The Phase-Volume Theory.—If into a given space small spheres of the same diameter are packed as closely as possible, the volume they will occupy is 74·048 per cent. of the total available volume, and this figure is a constant independent of the size of the spheres.[1] Ostwald used this fact as the basis for a theory of emulsions now known as the "phase-volume theory." According to him [2] two types of emulsion are only possible over a certain range of concentration. He did not agree that for any given volumes of oil and water *two* emulsions could be produced, depending on whether the oil was dispersed in the water or the water in the oil ; a system containing, say, 98 per cent. water and 2 per cent. oil could not be other than an emulsion of oil in water. In more definite terms, Ostwald formulated that an emulsion of one liquid in another was only possible when the volume concentration of the dispersed liquid was less than 74 per cent., the double series being possible only over the range of 25·96 per cent. to 74·04 per cent. by volume.

On this theory, when to an emulsion of oil in water oil is gradually added, the distance between the globules of oil becomes less and less, until finally the globules touch and coalesce, then becoming the continuous phase, enclosing globules of water. The inversion marks a "critical point." In the same way, if water be added to an emulsion of water in oil, another critical point can be reached. Theoretically the two critical points should coincide at 50 per cent. volume concentration, provided neither liquid affects the other. In practice Ostwald found no such coincidence, but an overlapping at about 48 per cent.

[1] *Vide* Bechold, Dede and Reiner, *Koll. Zeits.*, **28**, 18 (1921).
[2] *Koll. Zeits.*, **6**, 103 (1910) ; **7**, 64 (1910).

The phase-volume theory is unsound for several reasons, and, when formulated, quite ignored the very concentrated emulsions previously prepared by Pickering,[1] when even 99 per cent. by volume of oil was emulsified in dilute soap solution. Pickering, however, although preparing emulsions of great concentration, seemed inclined towards a volume limitation of emulsions. He called attention to the mathematical limit of 74·048 per cent. for closely-packed uniform spheres in a given space, but recognised that in emulsions the spheres were not uniform and were also separated by a film of appreciable thickness. He concluded therefrom that "there does not appear to be any reason why the ratio of the volume of oil to the total volume of emulsion should be of any particular magnitude." He added,

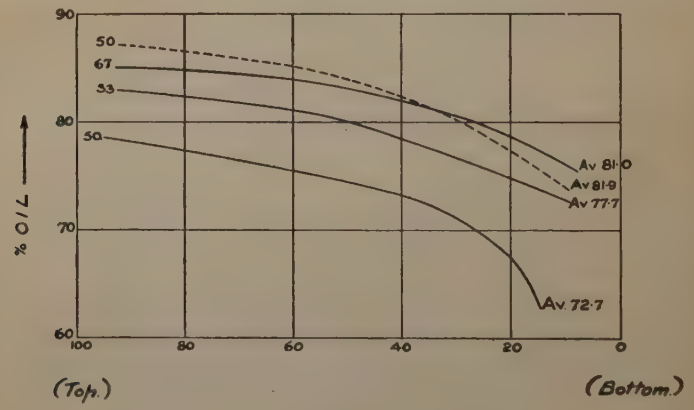


FIG. 3.

however, that in the majority of his emulsions the ratios actually found were from sixty-five to eighty-two for every 100 volumes of emulsion, and were independent of the initial proportions of oil and aqueous medium, provided the former did not exceed 80 per cent.

Pickering prepared stable emulsions of a mineral oil in a 1 per cent. soap solution, using oil volumes of 67 per cent., 50 per cent., and 33 per cent. respectively. After standing for twelve weeks, the supernatant emulsions ("cream") were

[1] *J. C. S.*, **91**, 2002 (1907).

analysed at intervals from top to bottom. The average oil contents in the "creams" were 81 per cent., 81·9 per cent., and 77·7 per cent. respectively. The volume percentage of oil diminished throughout from the top of the column of emulsion downwards, very slowly at first and more rapidly towards the bottom. Although the *initial* oil concentrations varied greatly, the final stable emulsions were surprisingly similar in composition. Fig. 3 expresses the results graphically. Repetition of the emulsification of 50 per cent. paraffin oil in 5·0 per cent. soap solution gave an emulsion very similar to that in 1 per cent. soap solution. With 50 per cent. paraffin in 0·2 per cent. soap solution much lower values were obtained, as shown in the lowest curve.

Bancroft [1] has discussed the work of Ostwald and Pickering, and pointed out that the two main assumptions in the phase-volume theory are untenable. Firstly, the drops in an emulsion are not all spherical and of equal size. Emulsion globules are capable of deformation of shape [2] owing to the properties of the enveloping film of the emulsifying agent.[3] Since the globules are of unequal size, it readily follows that the 74·048 per cent. volume limit of packing can be exceeded. Consider a system in which spheres of uniform size have been packed as closely as possible, occupying 74·048 per cent. of the available space. Then it is obvious that smaller spheres can be packed into the interstices, so that a larger volume percentage is now occupied. Mathematically, such packing into the interstices with smaller and smaller spheres is a variable function approaching, but not reaching, 100 per cent. as a limit.

The second assumption by Ostwald was that coalescence occurs when the emulsion globules touch, *i.e.*, after 74·048 per cent. by volume has been filled. The phases should now invert and a new continuous medium (oil) result. Owing to the presence of a surface film around the globules, coalescence does not necessarily follow touching. The globules may squeeze together until a vanishingly small space separates them. We

[1] *J. Phys. Chem.* **16**, 179 (1912).
[2] *Vide* Hatschek, *Koll. Zeits.*, **7**, 71 (1910).
[3] Cf. Briggs and Schmidt, *J. Phys. Chem.*, **19**, 496 (1915).

now know that dual emulsions can be made over any range of volume ratios. Very concentrated emulsions of both the oil-in-water and water-in-oil types have been prepared, and many examples of them will appear subsequently in these pages.

A study of inversion by the alteration of volume concentration in the case of olive oil emulsions has been made by Robertson,[1] special attention being given to " the influence of the proportion of alkali to the total volume of emulsion upon the critical ratio of water to oil at which the emulsion changed character and ceased to be an oil-in-water emulsion." Measured amounts of a very pure olive oil, containing only traces of free fatty acid,

Oil c.c.	Water c.c.	5N. Na OH. c.c.	Emulsion Characteristics.
99	0	1	Water-in-oil. Fluid. Yellow.
98	1	1	Ditto.
96	3	1	Ditto.
92	7	1	Water-in-oil. Yellow cream.
91	8	1	Water-in-oil.
90	9	1	Oil-in-water. Creamy white, very viscous.
89	10	1	Ditto. *Critical ratio* $= \frac{9{\cdot}5}{90{\cdot}5} = 0{\cdot}105$.

and of distilled water and NaOH, were shaken in special bottles under standard conditions. The resulting emulsions were examined under the microscope and by the use of Sudan III., an oil-soluble dye which helps to define the emulsion type.[2]

Robertson maintained the concentration of NaOH in the emulsions constant, increasing the concentration of water 1 per cent. in each succeeding experiment. He found that decreasing the proportion of water continued to give oil-in-water emulsions, until the proportion of water to oil reached a definite critical value at which the emulsion abruptly changes to the water-in-oil type. The critical ratio is defined as " the mean of the smallest ratio for which an oil-in-water emulsion can be obtained, and of the largest ratio for which a water-in-oil

[1] *Koll. Zeits.*, **7**, 7 (1910).
[2] See p. 104.

emulsion can be obtained." Thus, if a mixture containing 8 c.c. of water and NaOH gives an oil-in-water emulsion, whereas a mixture containing the same amount of NaOH, but 7 c.c. of water, gives the other type of emulsion, the critical ratio will be 7·5/92·5, since the total volume is constant, viz., 100 c.c. The error is, of course, 0·5/92·5. The results obtained by Robertson are typified in the table on p. 34. Throughout all the experiments 1 c.c. of NaOH solution was used, only the normality of the NaOH being varied for each series of emulsions. The results are summarised in the following table :—

Normality of NaOH.	Critical Ratio.
5 N	0·105
1 N	0·081
$\frac{1}{2}$ N	0·081
$\frac{1}{4}$ N	0·156
$\frac{1}{5}$ N	0·156
$\frac{1}{8}$ N	—[1]

Robertson found that the critical ratio of water to oil remained constant (0·08 for olive oil used) for alkali concentrations above N/200. When the alkali concentration fell below this limit, the amount of oil which could be emulsified in a given volume of water progressively diminished until, when the alkali concentration decreased to N/800, no stable emulsion of oil-in-water was possible. According to Robertson, the important factor throughout is the soap formed by the interaction of the alkali and the free fatty acid in the oil. He argued that while an excess of alkali was maintained the amount of soap present in the system would be constant. Below a limiting concentration of alkali fixed by the amount of free fatty acid present the soap formed would be insufficient to maintain an emulsion of oil in water, a large volume of oil dispersed as globules requiring more than the available amount of soap to form the protecting enveloping film. Such a

[1] No stable oil-in-water emulsion could be obtained.

quantity of soap, however, could envelop *water* in an oil medium, since there would be fewer globules to cover, and consequently the system changes over to the reverse type of emulsion.

Obviously a crucial point in this argument is the assumption that one and the same emulsifying agent can stabilise two emulsions of opposite type. Now the amount of free fatty acid in the oil was unknown in these experiments ; consequently the amount of soap formed is indeterminate, as is also its nature. Assuming sodium oleate was formed, why did Robertson obtain two types of emulsion with olive oil and this soap when in the case of benzene and kerosene emulsions sodium oleate only permits the oil-in-water type ? A possible explanation has been given by Bancroft,[1] who believes that sodium oleate is insoluble in kerosene or benzene,[2] whereas in high concentrations of olive oil the solubility of sodium oleate therein may prove a more important factor than the water solubility.

The results obtained might have been different if Robertson had altered his method of emulsification. Instead of shaking all the ingredients together in one operation, the large volume of oil could have been gradually added to the NaOH solution, emulsifying thoroughly after each addition. Undoubtedly more oil could thus have been dispersed in the aqueous phase and the critical ratio considerably diminished. When a large volume of one phase (*e.g.*, oil) and a small volume of the other (*e.g.*, water) are shaken in bulk together, the superior volume of the more abundant phase becomes an important factor.[3] From the purely mechanical aspect of the disintegration of particles, the water-in-oil type of emulsion is promoted. The manufacture of margarine provides an excellent example of this. About 80 per cent. by volume of oils are emulsified with 20 per cent. by volume of water and milk, which should promote the oil-in-water type of emulsion. If the oils are slowly run into the milk at about 30° C. with constant agitation, a thick custard-like emulsion of oil-in-milk results, characterised by considerable stability. If, however, both phases are placed in bulk in the churn and then agitated, an emulsion of milk-in-oil

[1] *J. Phys. Chem.*, **16**, 746 (1912).
[2] The insolubility of sodium oleate in benzene has been proved by Briggs.
[3] Cf. Sanyal and Joshi, *J. Phys. Chem.*, **26**, 481—6 (1922).

is obtained, but of poor stability. The same results can be reached if the milk be slowly added to the total volume of oils in the churn with constant agitation.[1]

Robertson's results are of much interest, inasmuch as he obtained two sets of emulsions, but they are prejudiced by the fact that the soap concentrations are unknown, and also by the fact that excess of free alkali may exert a particular influence on the system.

Bhatnagar [2] has also investigated the volume relations in emulsions of olive oil in alkali (KOH), and found that the volume percentage of 74·04 holds when the aqueous phase is very weakly alkaline (N/1,000 to N/500). With alkalis of greater concentration higher ratios were possible,[3] just as obtained by Robertson, but they broke up, yielding a stable cream, possessing the volume ratio 74 : 26. The phase ratios at the critical (inversion) point with different strengths of alkalis were found by Bhatnagar to be :—

KOH. c.c.	Olive Oil[4] c.c.	Strength of Alkali.	Volume Ratio at Inversion Point.
25	73·5	0·933 N/1,000	74 : 26
20	58·4	0·933 N/700	75·5 : 25·5
25	72·7	0·933 N/500	74·4 : 25·6
20	75·2	0·933 N/100	79 : 21
10	88·9	0·933 N/50	89 : 11

Bhatnagar believes that the change in a volume ratio with the more concentrated alkali is due to " the solid or gelatinous film " enveloping the oil globules, thus permitting squashing of the globules instead of coalescence on touching.

He next made emulsions containing the majority of the globules as equal spheres. Such were obtained by selecting from a new oil-in-water emulsion, the cream containing

[1] Cf. Clayton, *Trans. Farad. Soc.*, **16**, Appendix, p. 23 (1921).

[2] *J. C. S.*, **117**, 547 (1920).

[3] Cf. Fischer and Hooker, " Fats and Fatty Degeneration " (1917), p. 41. These investigators obtained stable emulsions up to 95 per cent. of cotton-seed oil in concentrated potassium soap solutions.

[4] Containing 0·5 per cent. free oleic acid.

approximately 74 per cent. of oil by volume. Small quantities (5 to 10 c.c.) were very vigorously agitated for several hours, until a microscope examination showed the particles to be small and of nearly equal size. Three such homogeneous emulsions were made, using different strengths of KOH, and known amounts were "broken" by a drop of strong HCl. The volumes of the two phases were then measured and checked against the values calculated on the assumption that closest packing has existed in the emulsions, in which case the ratio :

$$\frac{\text{Total volume of emulsion}}{\text{Volume of oil phase}} = 1{\cdot}35.$$

A very fair agreement was shown.

The results are given in the following table :—

Emulsion.	Total Volume c.c.	Strength of KOH.	Radii of Uniform Particulars.	Volume of Oil Phase.	
				Obs.	Calc.
				c.c	c.c.
1	7	0·933 N/500	0·0075 mm.	5·09	5·1
2	5	0·933 N/700	0·0070	3·7	3·69
3	5	0·933 N/1,000	0·0055	3·6	3·69

Hatschek[1] has pointed out that the stability of emulsions containing large percentages of dispersed phase is dependent on the phase ratio, and is generally not complete unless the figure corresponding to closest packing is approached. He also mentions the interesting theoretical possibility of an emulsion of two liquids having the same density ; such an emulsion should be quite stable, no matter what the value of the phase ratio.

The Viscosity Theory of Emulsions.—Two main points may be considered when discussing viscosity relations in emulsions : how viscosity influences stability or permanence and how the viscosity of the system as a whole depends on the degree of dispersion of the emulsified liquid.[2]

[1] *Brit. Assoc. Colloid Reports*, **2**, 17 (1918).
[2] See p. 122.

Hillyer [1] has pointed out the extent to which viscosity may be a factor in promoting emulsion stability, basing his views on earlier work by Plateau [2] in connection with foams. Plateau recognised that in bubbles and foams the two chief factors necessary are a certain degree of viscosity of the liquid used and a low air/liquid surface tension. The former tends to resist thinning of the liquid films to the rupture point, whilst a low surface tension is necessary because surface tension is the chief active force promoting thinning. Soap solutions readily yield permanent foams, owing to their low surface tension and their high viscosity. Plateau defines two viscosities for a liquid capable of foaming the internal viscosity due to molecular friction and the "superficial viscosity" which resists the movement of a body at the air/liquid interface. Stables and Wilson [3] confirmed the existence of this superficial viscosity in the case of a saponin solution,which frothed readily, although the surface tension was comparatively high. Ramsden [4] and others have extended this work, ascribing the results obtained to adsorption effects (see p. 51).

Hillyer [5] determined the surface tension and foaming capacity of a number of solutions in an approximate manner, and correlated the results with the viscosity of the solutions. He found that high viscosity alone will not account for stable foams; the surface tension must be low. Thus 50 per cent. aqueous glycerine and a 6 per cent. aqueous solution of gum acacia, each very viscous, but with relatively high surface tensions, do not yield permanent foams, whilst beer and milk, not so viscous, but with lower surface tension values, froth easily. Hillyer now raised the question: Can emulsification be explained by the viscosity of the emulsifying agent? Undoubtedly in certain cases, *e.g.*, pharmaceutical emulsions containing gums, high viscosity is a powerful aid in stabilising an oil-in-water type of emulsion. Viscosity, however, cannot be the only factor involved. This was proved by the fact that

[1] *J. Am. Chem. Soc.*, **25**, 513 (1903).
[2] *Pogg. Ann.*, **141**, 44 (1870).
[3] *Phil. Mag.* (5), **15**, 406 (1883).
[4] *Zeits. phys. Chem.*, **47**, 336 (1904).
[5] *Loc. cit.*

such viscous solutions as 50 per cent. glycerine and 6 per cent. gum acacia would not emulsify kerosene, or even so viscous an oil as cotton-seed oil. Dilute soap emulsions (*e.g.*, 1 per cent. Na oleate) with only a small viscosity are excellent emulsifiers for kerosene and cotton-seed oils. As a result of stalagmometric measurements with several solutions, including gum acacia, saponin, and soaps, and correlating these with the capacity of the solutions to emulsify kerosene and acid-free cotton-seed oil, Hillyer concludes : " Emulsification is due largely to the small surface tension between oil and the emulsifying agent, which allows the emulsifying agent to be spread out into thin films separating the oil droplets. The surface tension is not strong enough to withdraw the film from between the droplets except slowly, and if the emulsifying agent has great internal viscosity, or if great superficial viscosity is shown between the liquids, the thinning of the film is so slow that the emulsion is permanent."

Solutions of albumen and saponin (1 in 200) were observed by Hillyer to act as excellent emulsifying agents though the interfacial tension between the solutions and oil was not much lower than between water and oil. He accounted for the permanence of the emulsions obtained by using saponin solution and oil that " superficial viscosity " was the predominating factor, offering resistance to the withdrawal of the films of saponin from between the oil globules. The modern interpretation of this phenomenon is in the light of adsorption data (see p. 53), as was predicted by Höber.[1]

Marshall's work [2] on pharmaceutical emulsions led him to the conclusion that viscosity influenced the size of the emulsion globules and affected their permanency, but otherwise had no theoretical significance. Pickering,[3] after his successful experiments with certain insoluble powders as emulsifying agents, also pointed out that the viscosity factor had been over-emphasised. He stated that " dilute soap solutions are not very viscous, and yet their power of forming an emulsion may even be destroyed by increasing the concentration, and thereby

[1] " Physik. Chemie der Zelle und Gewebe," 3rd ed., p. 293 (1911).
[2] *Pharm. Journ.*, **28**, 264 (1909).
[3] *J. C. S.*, **91**, 2001 (1907).

the viscosity, above a certain point." White and Marden[1] have also shown that the viscosity of an emulsion affects the stability. Thus concentrated emulsions of a viscous oil like linseed oil in soap solutions were more stable than similar emulsions of kerosene, which is not so viscous.

The conclusion that *viscosity aids emulsification solely by virtue of the hindrance offered to coalescence of the dispersed globules*, and is not the *cause* of emulsification, has been accepted by the majority of investigators in this field. Recent work, however, by Holmes and Child[2] on gelatin as an emulsifying agent brings these authors to the conclusion that "the leading factor in oil-water emulsification with the aid of gelatin is viscosity, not the maximum, but the most favourable viscosity." The viscosity of gelatin solutions was varied by adding electrolytes such as sodium iodide, chloride, nitrate, and thiocyanate, which liquefy gelatin ; or sodium tartrate, citrate, and sulphate, which exert a solidifying action on gelatin. In all the experiments kerosene was emulsified in water to a concentration of 75 per cent. by volume. Eight different concentrations of gelatin were employed, ranging from 0·3 per cent. to 1 per cent., and these solutions contained the various salts to a concentration of 0·5 M. The stability (appearance) of the emulsions was noted after three or four months' standing.

The viscosities of the gelatin solutions containing the electrolytes were determined by a method admitted to yield rather rough results. The interfacial tensions were determined by the drop-pipette method. From their results Holmes and Child concluded that "viscosity plays the dominant part in the stability of gelatin emulsions," and not the interfacial tension. They were unable to prove the presence of a film of gelatin adsorbed at the surface of the kerosene globules, although Winkelbech[3] had shown that, when dilute solutions of gelatin were shaken with benzene, a film of gelatin appeared at the dineric interface.

This investigation seems rather unsatisfactory.[4] In the

[1] *J. Phys. Chem.*, **24**, 629 (1920).
[2] *J. Am. Chem. Soc.*, **42**, 2049—2056 (1920).
[3] *Zeits. angew Chem.*, **18**, 1953 (1906).
[4] Cf. Bancroft, *J. Ind.-Eng. Chem.*, **13**, 348 (1921).

first place the viscosity measurements are too rough, and, secondly, the drop-pipette method for measuring changes in the interfacial tension is very liable to errors with gelatin solutions, owing to the deformation of the drops, because of the adsorbed films which other workers have shown to be present at the interface, gelatin solution/kerosene. Briggs and Schmidt,[1] in particular, have drawn attention to the elasticity and strength of the adsorbed films when determining the drop numbers of benzene in aqueous gelatin.

The results of this investigation do not seem to support the theory of a favourable viscosity figure for emulsions of kerosene in gelatin, and the theory is not upheld that viscosity is the most important factor in the making and the stability of emulsions.

Clark and Mann,[2] in a thorough investigation of the emulsifying efficiencies of sucrose and certain colloids for benzene and kerosene emulsions, made a comparative study of the factors of viscosity and interfacial tension. With regard to sucrose they conclude: "The primary attribute is viscosity (usually maximum), even though there is evidence also of adsorption at higher concentrations upon the emulsion particles. On the other hand, viscosity cannot be considered the only prime requisite of an emulsifying agent, for though sugar furnishes a large and favourable viscosity, it does not compare as an emulsifying agent with even minute concentrations of other substances in which the viscosity factor is largely negligible." With dextrin, Clark and Mann found that although a 10 per cent. solution exhibiting maximum viscosity produced the heaviest cream in every emulsion, yet the most stable emulsions as measured by time of existence were produced by using solutions of 5 per cent. dextrin in 0·5 M sodium hydroxide, in which there is the maximum effect in reducing interfacial tension. Finally, since the best results were given by egg albumen solutions in which viscosity variations were unimportant, Clark and Mann concluded that the factor of predominating importance in emulsion stability is film formation (*vide* p. 55), and not viscosity.

[1] *J. Phys. Chem.*, **19**, 496 (1915).
[2] *J Biol. Chem.*, **52**, 157—182 (1922).

The Hydration Theory of Emulsions.—A theory of emulsification and emulsions has been proposed by Fischer, known as the hydration theory, according to which emulsions can only be produced when the liquid which is to become the continuous phase is all used in the formation of a hydrated compound of the emulsifying agent employed. On this view, for example, " when it is said that the addition of soap favours the formation and stabilisation of a division of oil in water, it really means that soap is a hydrophile colloid which, with water, forms a colloid hydrate with certain physical characteristics, and that the oil is divided in this. The resulting mixture cannot, therefore, be looked upon as a sub-division of oil in water, but rather as one of oil in a hydrated colloid." [1]

Such substances as acacia, soap, gelatin, casein, dextrin, agar-agar and albumens are considered to act as emulsifiers in virtue of their ability to form colloidal hydrated compounds. The emulsifying efficiencies of these substances vary, since their " hydratability " varies qualitatively and quantitatively. The hydrated emulsifier should preferably yield fairly viscous liquids " possessing good covering power together with great cohesiveness." [2]

The theory postulates that oil cannot be emulsified in a hydrated colloid until a certain minimum amount of water is present ; similarly, if too much water be present (exceeding the amount used in hydrating the colloid), no stable emulsion is possible.

Fischer's theory is open to several objections, and in the present writer's opinion is only partially true. It is quite correct to emphasise the importance of hydrophilic colloids for making emulsions of the oil-in-water type, but it is only logical to extend this and argue that oil-soluble colloids (hydrophobic colloids) promote the formation of the water-in-oil type of emulsions.[3] As regards the existence of the postulated hydrated colloid compounds, no evidence has been presented of a physico-chemical nature.

[1] Fischer and Hooker, " Fats and Fatty Degeneration " (N.Y., 1917), p. 5.
[2] *Loc. cit.*, p. 6.
[3] *Vide* Bancroft, " Applied Colloid Chemistry " (N.Y., 1921), p. 262.

The condition for the formation of water-in-oil emulsions has not been discussed by Fischer, except that in certain cases he believes there is a critical point at which any attempt to increase the oil content of the emulsions causes them to change over to emulsions of the water-in-oil type. The existence of concentrated emulsions such as were prepared by Pickering is quite ignored.

The essential difference between Fischer's theory and the present theory of an adsorbed film enveloping the emulsion globules is that in the former case the emulsifying agent is supposed to be evenly distributed throughout the aqueous phase as some sort of chemical compound with the water; the oil globules are dispersed in this aqueous phase because of its viscosity or "covering power." The modern theory believes that a *concentration* of the emulsifying agent occurs at the interface between the oil globules and the aqueous phase. Strangely enough, this very idea of adsorbed film protection of emulsion particles has to be resorted to by Fischer [1] in order to explain the formation of emulsions with finely-divided solids as emulsifying agents, and also to account for the stability of milk when diluted with water. Critical reading of Fischer's work does not establish a strong case for his hydration theory, which seems particularly one-sided in its treatment of emulsions.

In a study of the formation of pharmaceutical emulsions, Roon and Oesper [2] claim to have obtained experimental confirmation of Fischer's hydration theory. The so-called Continental method of making emulsions was investigated, the basis of which is that "all of the emulsifying agent is hydrated at one time and in the presence of the internal phase." Thus, 4 parts of oil and 2 parts of acacia are ground to a paste in a mortar; 3 parts of water are then added in bulk, and a thick creamy nucleus obtained by further trituration. This standard emulsion nucleus can then be diluted with water at will.

Roon and Oesper found that if these particular ratios were departed from, less stable or no emulsions resulted. They also

[1] "Fats and Fatty Degeneration," p. 53.
[2] *J. Ind.-Eng. Chem.*, **9**, 156—161 (1917).

found that previous hydration of the gum inhibited the formation of emulsions. They concluded that the mechanism of the Continental method of making emulsions was that "the agitation disperses the internal phase and the resulting droplets are immediately coated with hydrated colloid formed at the same instant, this coating being the *sine quâ non* of emulsification." Thus the presence of a hydration compound is essential to emulsification, and this acts most efficiently if it is produced simultaneously with the dispersion of the oil phase.

Briggs, Du Cassé and Clarke [1] repeated the experiments of Roon and Oesper, and pointed out that *shaking* the phases together gave greater latitude in emulsion formation than did trituration. Thus olive oil is easily dispersed in a solution of gum arabic, a previously hydrated compound. They then showed that olive oil could be readily dispersed in gum-arabic *solution* by triturating in a mortar, provided a finely-divided solid was present, *e.g.*, sand, quartz, glass, sugar, salt. It was found that these solids, which are easily wetted by water, are the most efficient, and they act best when suspended in the oil phase, since the aqueous phase tends to displace oil from the surface of the solid particles and so helps in the disintegration of the oil.

The same results were obtained using sodium oleate in place of gum arabic. Viscous oils, such as olive, linseed and pine oil, were more readily emulsified than were benzene, toluene, aniline, and chloroform.

Briggs, Du Cassé and Clarke abandon the hydration theory, believing that the essential factor in the "Continental" method is the presence of finely-divided solids, which serve to increase the area of the interface between oil and water or between oil and solution. The gum arabic functions in two ways: as a finely-divided solid, and as an emulsifying agent. When other solids are present the gum need only act in virtue of its second function, so that its aqueous solution is adequate.

The Surface Tension Theory of Emulsions.—Quincke [2] prepared emulsions of various oils in solutions of NaOH or gum

[1] *J. Phys. Chem.*, **24**, 147—160 (1920).
[2] *Wied. Ann.*, **35**, 589 (1888).

arabic, and showed that the interfacial tensions between the oils and these solutions were lower than those between the oils and pure water. Previous work by Brücke [1] and Gad [2] had shown that rancid oils, or oils containing free fatty acids, gave better emulsions in dilute solutions of borax or sodium carbonate than did purer oils. Gad even claimed that drops of oil containing free fatty acid gave spontaneous emulsions in 0·25 per cent. aqueous sodium carbonate. Spontaneous emulsions have also been obtained by Bhatnagar.[3] Quincke, commenting on the work of Gad, Brücke and himself, suggested that the ease of emulsification varied with the acidity and viscosity of the oil, the concentration of the alkaline solution, and the solubility in water of the resulting soap.

Later, Donnan [4] investigated the interfacial tensions between oils and alkaline solutions, using the drop-pipette,[5] by means of which he determined the number of drops of oil rising through the alkaline solution under standard conditions. The number of drops is, as a first approximation, inversely proportional to the ease of emulsification of the oil in the alkaline solution. The following figures relate to colza oil in aqueous caustic soda :—

Conc. of NaOH. (gram.-mols./litre).	Drop Number.
0	88
0·0005	115
0·0008	213
0·001	306
0·0011	430
0·0013	Stream.

Evidently, increasing the amount of NaOH in the aqueous phase causes a lowering of the interfacial tension. This lowering was shown by Donnan to be due to the formation of

[1] *Sitzungsber. Akad. Wiss. Wien.*, **61** (II.), 362 (1870).
[2] E. du Bois Reymond, *Arch. Anat. Phys.* (1878), 181.
[3] Private communication to the author. Cf. also Maday, *Zentr. Physiol.*, **27**, 381 (1914).
[4] *Zeits. phys. Chem.*, **31**, 42 (1899).
[5] See p. 102.

soap, since a carefully purified neutral oil gave the same drop number in NaOH as in water.[1] Thus :—

Oil.	Reaction.	Drop Number in Water.	Drop Number in N/1000 NaOH.
Commercial olive oil .	Acid.	58	331
Purified olive oil .	Neutral.	58	58

In order to prove that soap was not formed by a surface saponification of glyceride, Donnan employed a paraffin hydrocarbon oil. Thus :—

Oil.	Acidity.	Drop Number.	
		Water.	N/100 NaOH.
Hydrocarbon.	Neutral . . .	47	52·7
Hydrocarbon.	0·6 per cent. commercial stearic acid added .	48·5	320·0

Donnan now investigated the dispersion in NaOH of hydrocarbon oils containing different members of the fatty acid series, and found that the interfacial tension diminution was peculiar to the higher fatty acids, from lauric acid onwards. Drop numbers of hydrocarbon oils containing 0·7 per cent. free fatty acid had the following values :—

Acid.		Drop Number in Water.	Drop Number in N/1000 NaOH.
(C_1)	Formic . .	34	37
(C_2)	Acetic . .	38	38
(C_4)	Butyric .	38	35
(C_8)	Caprylic .	44	47
(C_{12})	Lauric . .	43	82

[1] *Vide* Rachford (*Journ. Physiol.*, **12**, 72 (1891)), who found that a pure neutral oil could not be emulsified in dilute sodium carbonate solution.

Having suggested that emulsification was intimately connected with the formation of a layer of soap solution at the oil-water interface, Donnan [1] investigated the relation between the concentrations of solutions of the sodium salts of the various fatty acids, and the interfacial tension between these solutions and a high-grade hydrocarbon oil containing only 0·1 per cent. free fatty acid. The interfacial tensions were again measured by the drop-pipette and calculated on the basis that the interfacial tension between the oil and water = 1. The following results were obtained :—

Sodium Salt of	Interfacial Tensions at Concentrations of								
	0	N/400	N/200	N/100	N/80	N/40	N/25	N/20	N/10
Acetic acid .	1	—	—	0·995	—	0·970	—	0·937	0·876
Propionic acid	1	—	—	—	—	0·946	—	0·901	0·827
Butyric acid .	1	—	—	—	—	0·945	—	0·909	0·856
Valeric acid .	1	—	—	—	—	—	0·946	0·908	0·821
Heptylic acid .	1	—	—	—	—	0·939	—	0·909 ?	N (0·098) 0·754
Caproic acid .	1	—	—	—	0·947	0·921	—	0·869	0·780
Caprylic acid .	1	0·962	—	0·895	—	0·797	—	—	—
Capric acid .	1	—	—	—	0·835	0·730	0·630	—	Stream
Nonylic acid .	1	0·911	0·856	0·798	0·753	0·656	—	—	—

The figures for sodium laurate and myristate were as follows :—

Sodium laurate :					
Concentration .	0	N/200	N/160	N/100	N/80
Interfacial tension	1	0·698	0·646	0·532	0·474
Sodium myristate :					
Concentration .	0	N/1,600	N/800	3N/1,600	N/400
Interfacial tension	1	0·872	0·753	0·675	0·585

The above results are expressed graphically in Figs. 4 and 5. The ordinates in Fig. 4 are the relative interfacial tensions, the abscissæ being concentrations of the sodium salts. Fig. 5 expresses the relation between the relative interfacial tensions

[1] Donnan and Potts, *Koll. Zeits.*, 4, 208—214 (1910).

and the molecular weights of the fatty acids concerned. Sodium caprylate (C_8) is the first to show a marked effect in lowering the interfacial tension, the effect then increasing rapidly with rise in the molecular weight.

Donnan and Potts concluded that the sodium salts of the higher fatty acids were adsorbed (following Gibbs' rule) at the separating boundary between the oil and solution.[1] This is the basis of the modern theory of emulsions discussed in

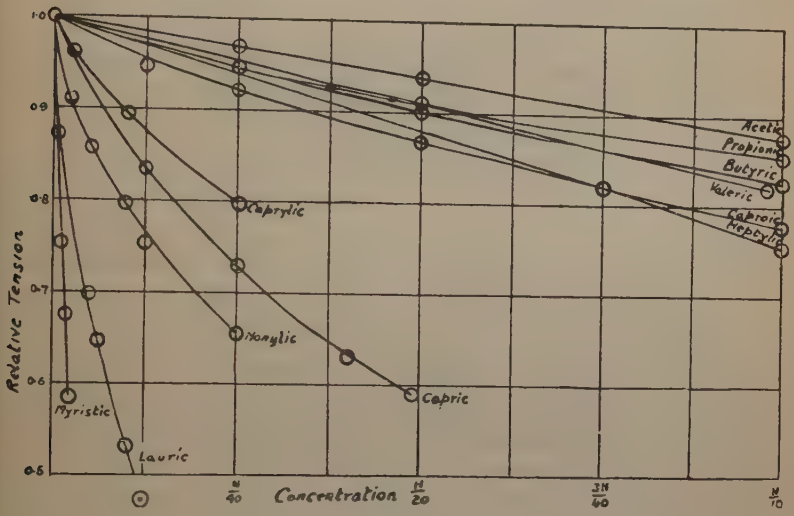


FIG. 4.

Chapter VI. It was pointed out that Mayer, Schaeffer and Terroine [2] found, by an ultramicroscope examination of the sodium salts of the fatty acids, that the lower members gave ordinary aqueous solutions, whilst the solutions of sodium heptylate, caprylate and laurate were colloidal. The characteristics of soap solution first appear in the series with sodium caprylate becoming very pronounced with sodium laurate.

Donnan and Potts now investigated the emulsifying power of the various sodium salts with respect to a pure hydrocarbon oil. The sodium salts of the lower fatty acids gave no emulsions, sodium caprate and nonylate gave dilute emulsions, whilst

[1] *Loc. cit.*, pp. 211, 214.
[2] *Comptes rend.*, **146**, 484 (1908).

sodium laurate and myristate promoted fairly satisfactory emulsification. For each salt capable of promoting emulsification there appeared an optimum concentration where the emulsifying power was a maximum. There seems to be a salting-out action, possibly due to the positive sodium ions coagulating the negatively-charged oil drops. Evidently, up to sodium laurate, ineffective emulsifying properties are exhibited because the coagulating action of the sodium ions exceeds the effect of the emulsifying tendency due to interfacial tension lowering.

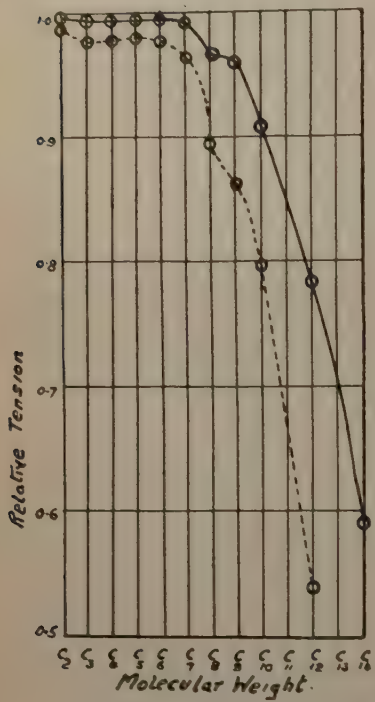


Fig. 5.

As a result of their work, Donnan and Potts concluded that "changes in the interfacial tension at the boundary oil/water are connected with changes in electrical potential, in which the selective adsorption of ions probably plays a part." Later work by Clowes and Bhatnagar amply verified this conclusion.[1] Donnan and Potts also concluded that emulsified globules of oil were surrounded by a "very viscous or possibly gelatinous film which offers resistance to the coalescence of the globules." Indications of such film formation around oil globules emulsified in solutions of bile salts were obtained by Lewis.[2] This film is the result of adsorption consequent upon the lowering of the interfacial tension at the boundary oil/water. A somewhat similar conclusion has also been reached by Hillyer,[3] who recognised that emulsification was intimately connected with

[1] See p. 97.
[2] *Phil. Mag.* (April, 1908), p. 499.
[3] *J. Am. Chem. Soc.*, **25**, 513 (1903).

"a small surface tension between oil and the emulsifying agent." He did not, however, realise the fundamental nature of the facts involved and their relation to the Gibbs rule. Later work in Donnan's laboratory by Lewis, Ellis, Powis and Barker, amplified and extended the surface tension theory, and correlated it with adsorption, electrical charges and coagulation of emulsions.

Ramsden [1] arrived at conclusions very similar to those of Donnan by an entirely different avenue. He demonstrated that many colloidal solutions and suspensions could be coagulated by mere agitation, forming fibrous or gelatinous membranes of an irreversible character. Regarding emulsions, Ramsden believed that one of the most important factors involved was the presence of a highly viscous gelatinous film enveloping the oil globules, this film being the result of adsorption, accompanied by a diminution of surface energy at the oil/water interface.

In 1910, Pickering [2] published a paper in which he asserted that, while high viscosity and low surface tension are undoubtedly favourable to emulsification, the most important factor is the presence of finely-divided particles, insoluble in the external phase, which coat the oil globules, and so prevent their coalescence.[3] Donnan [4] criticised this "solid particle theory," stating that Pickering apparently did not connect adsorption with the lowering of surface tension, and that electrical effects were entirely overlooked.

Pickering's emulsions, however, although in many cases stabilised by insoluble powders, do not form exceptions to Donnan's surface tension theory, since the solid particles would not go to the oil/water interface unless this new arrangement was accompanied by a lowering of the oil/water interfacial tension.

Pickering stated that solid emulsifiers must be of a certain definite range of grain,[5] non-crystalline, and more readily wetted by water than by oil.

[1] *Proc. Roy. Soc.* (A), **72**, 156 (1903); *Zeits. phys. Chem.*, **47**, 336 (1904).
[2] *Koll. Zeits.*, **7**, 11 (1910).
[3] Similar views in favour of his "Particulate Theory" of emulsions were advanced by Marshall (*Pharm. Journ.*, **28**, 264 (1909)). He stated, however, that the theory only held in certain instances.
[4] *Koll. Zeits.*, **7**, 214 (1910).
[5] *J. S. C. I.*, **29**, 129 (1910).

CHAPTER IV

ADSORPTION AT LIQUID-LIQUID INTERFACES

When two immiscible liquids are in contact the boundary surface between them is referred to as the liquid-liquid interface, or the dineric interface. This is not an absolutely distinct line of demarcation, but rather a very attenuated layer (a few millionths of a centimetre deep), due to the interpenetration of both phases. In emulsions, whether of the oil-in-water or water-in-oil type, there exists a relatively large interfacial separating layer, the area of which increases very rapidly with increasing subdivision of the dispersed phase.

The surface tension at the boundary between two immiscible liquids is termed the interfacial tension. It can be shown on thermodynamical grounds that, if a third substance now be added which will affect the value of the interfacial tension, concentration phenomena appear, *i.e.*, the concentration of the added substance will be different in the main bulk of the continuous phase from what it is at the interfacial separating surface. The most stable arrangement accompanying interfaces in general is that the surface energy should be a minimum. Consequently, if a dissolved substance raises the potential energy at the interface, it will tend to leave that interface ; if it diminishes the potential energy, then it will concentrate at the interface. This is in accordance with the Le Chatelier-Braun principle of " mobile equilibrium."

An equation connecting concentration of the solute at the interface with the surface energy has been given by Willard Gibbs [1] as follows :—

$$U = -\frac{c}{RT} \cdot \frac{dS}{dc},$$

where U is the excess concentration at the interface in

[1] *Scientific Papers*, Vol. I., pp. 219 *et seq.* (1906) ; cf. also Thomson, " Applications of Dynamics to Physics and Chemistry " (1888), p. 190.

grams/c.c., c the concentration of the solute in the bulk of the solution, and S the interfacial tension in dynes/cm.

Various derivations of this famous equation have been given by Thomson,[1] Milner,[2] Freundlich,[3] Harlow and Willows,[4] Porter,[5] Michaelis,[6] Morton,[7] and Harkins.[8] The following simple development is due to Ostwald.[9]

Let a solution whose surface is w contain 1 mol excess of solute concentrated in that surface, and let S be the surface tension. If a very small amount of solute enters the surface from solution and causes a decrease in the surface tension by dS, the surface energy change will be wdS. This change of energy must be equal to the change in energy when the same quantity of solute leaves the interior of the solution in opposition to the osmotic pressure due to this small mass of dissolved substance. If unit weight of solute is contained in a volume v of solution and the change in osmotic pressure after removal of the small mass of solute is dp, the energy change is vdp; then

$$wd\mathrm{S} + vdp = 0.$$

Assuming the gas law holds in the case of this dilute dolution,

$$v = \mathrm{RT}/p,$$

so that

$$wd\mathrm{S} + \frac{\mathrm{RT}}{p}\,dp = 0$$

or

$$\frac{d\mathrm{S}}{dp} = -\frac{\mathrm{RT}}{pw}.$$

Now p is directly proportional to the concentration c.

Therefore

$$\frac{d\mathrm{S}}{dc} = -\frac{\mathrm{RT}}{cw}.$$

If U is the excess concentration of solute in unit surface, then, since w is the surface containing 1 mol excess of solute, U equals $1/w$, whence

$$\mathrm{U} = -\frac{c}{\mathrm{RT}} \cdot \frac{d\mathrm{S}}{dc}.$$

1 "Applications of Dynamics to Physics and Chemistry," p. 190.
2 *Phil. Mag.*, **13**, 96 (1907).
3 "Kapillarchemie" (1909), p. 50.
4 *Trans. Farad. Soc.*, **11**, 53 (1915).
5 *Ibid.*, **11**, 51 (1915).
6 "Dynamik der Oberflächen" (1909), p. 20.
7 *Phil. Mag.* (April, 1908), p. 504.
8 *J. Am. Chem. Soc.*, **39**, 551 (1917).
9 "Outlines of General Chemistry," 3rd Eng. ed. (1912), p. 499

Since $\frac{dS}{dc}$ is the differential co-efficient of the function connecting interfacial tension and concentration, it follows that $\frac{dS}{dc}$ is positive when the solute increases the interfacial tension, and negative when it decreases it. Consequently, U is positive when the added substance lowers the interfacial tension, *i.e.*, the added substance will be adsorbed at the boundary surface if by its adsorption the interfacial tension is reduced.

The earlier work on the concentration of solutes at boundary surfaces was done in connection with foams, *i.e.*, at the liquid/air interface.[1] Ramsden[2] in 1894 had shown that agitation of various proteid solutions caused separation of part of the dissolved proteid as fibrous or membrano-fibrous solids; egg-albumin, for example, could be coagulated and totally removed from solution by sufficient agitation. Numerous solutions and suspensions were similarly made to yield solid free-surface coatings which in some instances were not resoluble in the mother liquor. Ramsden showed that such spontaneous de-solutions of previously dissolved matter at the free surface was due to the accumulation at the surface of the solute owing to its being adsorbed there because of the lowering effect on the surface tension. Agitation or shaking simply served to increase and expose the free surface.

Ramsden[3] then showed that in the case of several persistent emulsions actual solid membrane separated out at the liquid/liquid interfaces, *e.g.*, between olive oil and saponin solutions. The membrane manifested itself in such phenomena as (1) the intense viscosity at the interface, (2) the deformed appearance of otherwise spherical dispersed globules, and (3) the appearance of semi-opaque membranes when the separating surfaces were appropriately deformed. It was concluded that "the persistence of many emulsions is determined largely, among other factors, by the presence of solid or highly viscous matter at the

[1] Hall, *Proc. Roy. Soc.* (*Dub.*), **9**, 56 (1899); Benson, *J. Phys. Chem.*, **7**, 532 (1903); Zawidzki, *Zeits. phys. Chem.*, **35**, 77 (1900); **42**, 612 (1903); Metcalfe, *ibid.*, **52**, 1 (1905); Rohde, *Drude's Ann.*, **19**, 935 (1906).

[2] *Archiv. f. Anat. u. Physiol.*, 517—534 (1894); *Zeits. phys. Chem.*, **47**, 336—346 (1904); *Trans. Liv. Biol. Soc.*, **33**, 3—24 (1919).

[3] *Proc. Roy. Soc.* (A), **72**, 156 (1903).

interfaces of the two liquids," and that " accumulation of solid matter at the interfaces of the above emulsion-pairs occurs because the surface energy is thereby diminished."

Similar enveloping films in emulsions have been visualised by Clowes [1] with olive oil emulsions, by Clark and Mann [2] with emulsions stabilised with egg-albumin, and by Holmes and Cameron,[3] who dispersed water in a mixture of amylacetate and benzene, using cellulose nitrate as the emulsifying agent. Tough elastic films were clearly seen around the water globules.

Concentration of Sod. Glycocholate.	Relative Tension.	Tension dynes/cm.
Per cent.		
0	1·000	48
0·0312	0·633	30·38
0·0625	0·549	26·35
0·125	0·404	19·39
0·165	0·341	16·37
0·200	0·307	14·73
0·250	0·272	13·05
0·300	0·245	11·76
0·330	0·241	11·57
0·360	0·230	11·04
0·400	0·225	10·80
0·500	0·219	10·51

Wiegner [4] has demonstrated the existence of adsorbed films around the fat globules in homogenised milk, whilst Sheppard obtained micro-photographs of semi-elastic membranes in certain " aged " emulsions.

Whilst the qualitative side of the subject is well established, the quantitative results have not been so satisfactory.

Lewis [5] investigated the system hydrocarbon oil/aqueous solution of sodium glycocholate, determining the mass of solute adsorbed per cm.^{2} of oil surface and the interfacial tension

[1] *J. Phys. Chem.*, **20**, 407 (1916).
[2] *J. Biol. Chem.*, **52**, 182 (1922).
[3] *J. Amer. Chem. Soc.*, **44**, 66 (1922).
[4] *Koll. Zeits.*, **15**, 105 (1914); cf. Storch, *Analyst*, **22**, 197 (1897); Bechold, " Colloids in Biology and Medicine " (N.Y.), 1919, p. 346.
[5] *Phil. Mag.* (April, 1908), p. 499.

between the oil and solution. The interfacial tension was determined by the drop-pipette method for various concentrations of the solute, and the relative tensions so observed were converted into absolute values (dynes/cm.).

The results given in the table on p. 55 were obtained for a pure hydrocarbon oil and solutions of sodium glycocholate. The results are plotted in Fig. 6, the ordinates being tensions

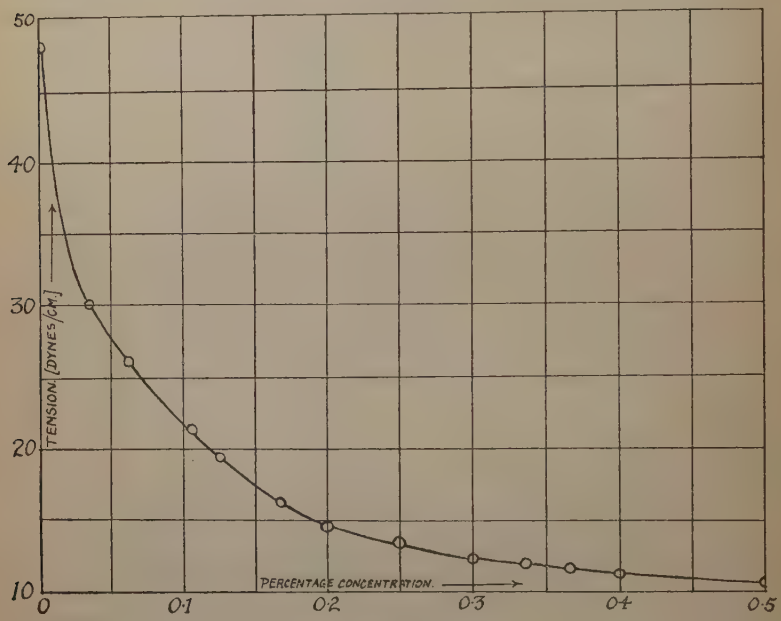


Fig. 6.

in dynes/cm., and the abscissæ the per cent. concentrations of sodium glycocholate. The value $\frac{dS}{dc}$ can be obtained for any concentration by taking the value of the trigonometrical tangent to the curve at the desired concentration.

Having secured data for determining $\frac{dS}{dc}$, the next step was to determine U, the *excess* concentration of sodium glycocholate in the oil/solution interface. A typical example from Lewis' paper shows the procedure followed.

Two hundred and fifty cubic centimetres of a 0·317 per cent. solution of sodium glycocholate was shaken with 0·160 c.c. of oil for twelve hours, and then allowed to stand for eighteen hours. A drop of emulsion was then examined under the microscope and the average radius of the oil globules ascertained. Thus :

$$\text{Average radius} = 0{\cdot}0000425 \text{ cm.}$$

$$\therefore \text{ volume of one globule} = \frac{4}{3} \times 3{\cdot}1416 \times (0{\cdot}0000425)^3 \text{ c.c.,}$$

since the total volume of oil emulsified was 0·160 c.c.

$\therefore$ Total number of globules $= 4{\cdot}97 \times 10^{11}$.

Now the surface area of one globule $= 4 \times 3{\cdot}1416 \times (0{\cdot}0000425)^2$ cm.^{2}

$\therefore$ Total adsorbing surface area = 11,058 cm.^{2}

To estimate the quantity of sodium glycocholate adsorbed, the drop number of the solution was determined before and after emulsification with oil (assuming the oil globules do not affect the drop number) and the concentrations of sodium glycocholate read off from the graph. Thus :

	Before.	After.
Drop number . =	531	507
Interfacial tension =	11·57 dynes/cm.	12·12 dynes/cm.
Concentration . =	0·317 per cent.	0·290 per cent.

$\therefore$ The fall in concentration = 0·027 per cent., *i.e.*, 0·067 gram for the 250 c.c. of solution employed. Hence the mass adsorbed per sq. cm., *i.e.*, U $= 0{\cdot}067 \times 11{,}058$

$$= \underline{5{\cdot}9 \times 10^{-6}} \text{ gram per cm.}^2$$

Another test with a solution of sodium glycocholate of 0·2 per cent. initial concentration gave U $= \underline{4{\cdot}7 \times 10^{-6}}$ gram per cm.^{2}

The calculated value of U is $-\frac{c}{RT} \cdot \frac{dS}{dc}$.

Taking the second experiment, the concentration $c = 0{\cdot}2$ per cent., *i.e.*, 0·002 gram/c.c. The temperature was 289 abs. = T. R is the gas constant.

For 1 gram of solute, $R = \frac{2 \times 4{\cdot}2 \times 10^7 \text{ ergs}}{\text{molar weight}}$.

The molar weight of sodium glycocholate in aqueous solution was found to be 140.

The co-efficient $\frac{dS}{dc}$, read from the graph at the point where c is 0·2 per cent., gave

$$\frac{dS}{dc} = \frac{9{\cdot}5 \text{ dynes}}{{\cdot}002 \text{ gram/c.c.}} = 4{,}750.$$

$$\therefore -\frac{c}{RT} \cdot \frac{dS}{dc} = \frac{{\cdot}002 \times 4750 \times 140}{2 \times 4{\cdot}2 \times 107 \times 289}$$

$$= \underline{5{\cdot}5 \times 10^{-8}} \text{ gram per cm.}^2$$

A serious discrepancy exists between the theoretical and experimental results, there being nearly eighty times more adsorption in practice than was calculated from theory. Lewis also observed similar discrepancies in the quantitative adsorption of dyestuffs of the oil/water interface. In a later paper, Lewis [1] has collected his results in the following table :—

Substance.	Adsorption per cm.² of the substance assumed to be in the form of undissociated salt or in chemically equivalent ionic proportions.	
	Found Value.	Calculated Value.
	grm.	grm.
Sodium glycocholate .	5×10^{-6}	7×10^{-8}
Congo red . . .	$3{\cdot}7 \times 10^{-6}$	$1{\cdot}1 \times 10^{-7}$
Methyl orange . .	$5{\cdot}5 \times 10^{-6}$	$1{\cdot}2 \times 10^{-7}$
Sodium oleate . .	10^{-6}	10^{-8}
Caustic soda . .	$1{\cdot}5 \times 10^{-7}$	$7{\cdot}5 \times 10^{-9}$

The substances exhibiting wide variations from the values calculated from the Gibbs equation are known to yield colloidal solutions in water, especially when concentrated. The Gibbs equation only applies to true (molecular) solutions, since it

[1] *Phil. Mag.* (April, 1909), p. 494.

is derived on the strict assumption that there is only one adsorbable component, which must form with the solvent *one phase* only. Lewis [1] suggested the now generally accepted view that the discrepancies are due to the fact that these colloidal substances form a gelatinous or semi-solid skin around the oil globules. In deriving his equation Gibbs not only assumed that the solute and solvent must form one phase, but also assumed that adsorption of solute would not cause any change in the energy of the molecules of the solvent in the surface layer; such energy changes, however, are known to take place. Another assumption was that the liquid in the surface layer has the same density as in the bulk of the solution. It is quite probable, however, that a change in density does occur, owing to the high concentration and compressibility of the liquid in the surface layer.[2]

Besides the Gibbs equation it is necessary to mention the widely-used adsorption isotherm, associated more particularly with the name of Freundlich.[3] This is a purely empirical relation, frequently, though erroneously, referred to as the adsorption exponential equation. If

m = mass of adsorbing material in grams,
x = amount of solute adsorbed by this mass,
C = the final or equilibrium concentration of the solute,

then $$\frac{x}{m} = a\mathrm{C}\frac{1}{n},$$

where a and n are constants ($n>1$) for a given solute and adsorbing material (adsorbent). Since the exponent $\frac{1}{n}$ is a constant, the equation is that of a general parabola. For representing experimental results on adsorption it is usual to express the equation in a logarithmic form, viz.,

$$\log x - \log m\ . = \frac{\log \mathrm{C}}{n} + \log a.$$

This is the equation of a straight line; the curve obtained by

[1] *Vide* criticism by Ferguson, *Manchester Memoirs*, **65** (4), 13 (1921).
[2] Lewis, *Phil. Mag.* (April, 1909), p. 490; cf. also Hatschek and Willows, "Surface Tension and Surface Energy" (1915), pp. 48—49.
[3] "Kapillarchemie" (1909), p. 147

plotting log x against log C, the two variables, is a straight line.

One important fact is immediately evident from inspection of the adsorption isotherm, or " concentration function " as it is now frequently termed, viz., the extent of adsorption is relatively more pronounced in dilute solution, the amount adsorbed increasing with, but more slowly than, the concentration. Adsorption at interfaces, whether air/liquid or liquid/liquid, takes place very rapidly, and in certain instances the resulting adsorbed film becomes saturated at surprisingly low concentrations of the solute.

Other formulæ have been given by various investigators, and certain peculiarities and anomalies in connection with adsorption pointed out.[1] The adsorption isotherm concerns us here only in so far as it has been applied in investigations on emulsions.

Briggs [2] studied the adsorption of soap in the interface between benzene and water, with the object of ascertaining the amount of soap required to produce protecting films in emulsions of benzene in soap solution. Emulsions of benzene were prepared in sodium oleate solutions and then homogenised. The sodium oleate content of the solution before and after emulsification was determined by titrating 10 c.c. with $\frac{N}{20}$ HCl under identical conditions, using methyl orange as indicator. Briggs assumed that the decrease in alkali content following emulsification was a measure of the sodium oleate adsorbed by the benzene globules. This assumption may not be strictly true, as possibly the difficulty-soluble *acid* sodium oleate produced by hydrolysis may be a factor in emulsification.[3] This, of course, will not affect the general question of adsorption. Briggs' results, however, are probably low, since he calculates for the adsorption of anhydrous sodium oleate, whereas it is very probable that in the benzene-water interface sodium oleate is hydrated.

[1] *Vide* Bancroft, " Applied Colloid Chemistry " (1921), p. 100.
[2] *J. Phys. Chem.*, **19**, 210—231 (1915).
[3] Cf. Pickering, *J. C. S.*, **91**, 2013 (1907).

Seven sets of emulsions were homogenised and allowed to stand twenty-two hours, when 10 c.c. of the aqueous layer were removed for titration with $\frac{N}{20}$ HCl. The soap solutions were made by diluting a stock solution containing 10 per cent. sodium oleate in water. In all cases 60 c.c. of soap solution and 90 c.c. benzene were used. The following results were obtained :—

Emulsion.	Soap Concentration. Number of c.c. of Stock Soln./500.	c.c. $\frac{N}{20}$ HCl.		Difference.
		Before Emulsifying.	After Emulsifying.	
1	5	0·54	0·38	0·16
2	10	1·02	0·75	0·27
3a	25	2·40	1·98	0·42
3b	25	2·39	2·05	0·34
4a	50	4·47	4·10	0·37
4b	50	4·43	3·97	0·46
5	100	9·25	8·79	0·46
6	150	13·81	13·34	0·47
7	180	17·01	16·50	0·51

The curve obtained by plotting the "difference" values as ordinates and the number of cubic centimetres of HCl before emulsification as abscissæ showed much similarity to the adsorption isotherm. The quantitative value of the curve was unsatisfactory, owing to the lack of further values for dilute solutions of the soap.

Briggs now examined the curve given by the logarithmic equation :

$$\log \frac{x}{m} = \log a + \frac{1}{n} \log C.$$

Where C = equilibrium concentration of sodium oleate in grams/litre.

$\frac{x}{m}$ = grams sodium oleate adsorbed per litre of benzene.

If $\log \frac{x}{m}$ be plotted as ordinates and log C. as abscissæ, then the slope of the curve gives the value for $\frac{1}{n}$, and the ordinate-intercept gives log a, whereby the constants are readily computed from the experimental data. Thus :—

C.	$\frac{x}{m}$ (observed).	Log C.	Log $\frac{x}{m}$.	$\frac{x}{m}$ (calc.).
grs.	grs.			grs.
0·60	0·17	— 1·778	— 1·226	0·29
1·18	0·28	0·072	— 1·453	0·32
3·18	0·40	0·502	— 1·601	0·38
6·36	0·44	0·804	— 1·645	0·42
13·85	0·48	1·142	— 1·684	0·48
21·03	0·49	1·323	— 1·694	0·51
26·01	0·54	1·415	— 1·729	0·53

Excluding the first two pairs of values of log C. and log $\frac{x}{m}$, the logarithmic curve shows approximately a straight line, whence the constants were calculated as $a = 0{\cdot}316$, and $\frac{1}{n} = 0{\cdot}756$. Briggs concluded that the amount of soap adsorbed agrees fairly well with that required by the Freundlich equation, except for dilute soap solutions, where the adsorption is less than that calculated. Although such a discrepancy might be accounted for by consideration of the hydrolysis of sodium oleate in dilute solutions,[1] further work is necessary.

Other workers have also used the logarithmic curve in presenting evidence for adsorption phenomena in emulsions. Clowes,[2] in particular, used it in his studies on olive oil emulsions. Thus he found that the ratio between the drop number of olive oil and the concentration of soap or NaOH, in which the oil was to be emulsified, was invariably logarithmic. He also found that the addition of varying proportions of NaCl to an

[1] Cf. Kahlenberg and Schreiner, *Zeits. phys. Chem.*, **27**, 552 (1898).
[2] *J. Phys. Chem.*, **20**, 407 (1916).

emulsion of the oil-in-water type lowered the concentration of OH ions in the aqueous phase in a logarithmic ratio.

Nugent [1] claims to have measured the rate at which an emulsifier is adsorbed at an interface. He found that, when emulsions of benzene (50 per cent. volume concentration) in 0·4 per cent. gelatin solutions were treated with NaOH, separation of benzene took place. This separation began at once when NaOH was added to the freshly-made emulsion, but for emulsions which had been allowed to stand for some time an inhibition period was noted before separation began. Thus, taking an emulsion and adding NaOH, so as to produce in the emulsion a concentration of 0·5 N. NaOH, the following results were obtained :—

Age of Emulsion before adding NaOH.	Inhibition Period.
Hours.	Minutes.
0	0
2	35
6	45
12	55
24	60
48	70
72	75

The results are plotted in Fig. 7, and the smooth curve is parabolic in shape. A straight line is obtained if the logarithms of the "age" are plotted against the logarithms of the inhibition period.

Nugent believes that, after the emulsion is produced, adsorption of gelatin at the interface benzene/water still continues, so that the stability of the emulsion will increase with its age. Addition of NaOH in some way removes the gelatin, layer by layer. The inhibition period may be regarded as the time taken for the NaOH to remove the adsorbed layers of gelatin. On this view, the age of the emulsion may be referred to as the time required to produce a given amount of adsorption.

[1] *Trans. Farad. Soc.*, **17**, 703—7 (1922).

Nugent calculates that the rate of adsorption depends directly upon the amount already adsorbed and inversely upon the age of the emulsion, *i.e.*, upon the time.

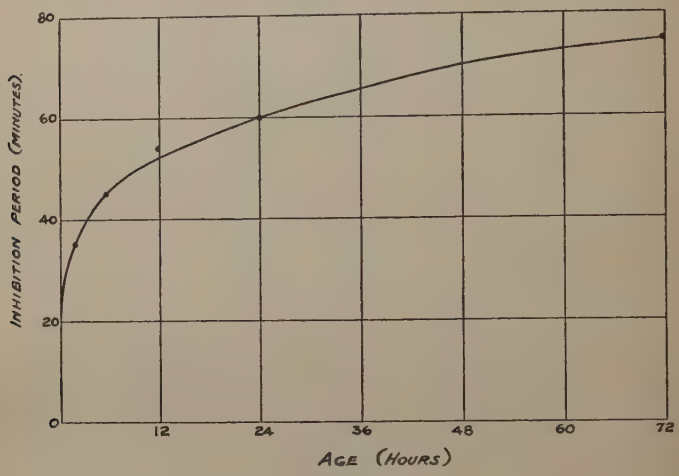


FIG. 7.

The "limiting inhibition period" was determined for benzene emulsions in various concentrations of gelatin solutions, and refers to the inhibition period, which no longer increases with the age of the emulsion. Thus :—

Concentration of Gelatin Solution employed.	Limiting Inhibition Period.
Per cent.	Minutes.
0·1	0
0·12	5
0·15	15
0·2	25
0·4	75

Readings were taken to the nearest five minutes. The graph of the results is a straight line. "The significance of the limiting inhibition period on the basis of the view put forward is that we are here dealing with the final equilibrium quantity

adsorbed from the corresponding concentrations in the bulk of the continous phase."

Nugent's results are very interesting, and certainly demand further investigation. The nature of the action of dilute NaOH on gelatin under these conditions requires elucidation, as does also the question as to whether the gelatin is irreversibly "precipitated" in the adsorbed film.[1] The fact that with 0·1 per cent. gelatin solutions no inhibition period was noted under the conditions of this investigation is especially important, since it suggests a way towards determining the dimensions of such adsorbed films around the benzene globules.

Another important point raised by Nugent's work is the effect of ageing of the gelatin on emulsion stability. He finds the protective action of the gelatin increases with the age of the emulsion. Elliott and Sheppard[2] found that the gold number of gelatin solutions increases with the age of the solutions, *i.e.*, the protective power of the gelatin gradually decreases, probably owing to an agglomeration of amicrons to form larger particles, whose protective capacity is less than that of finer gelatin particles.[3] It may be that the thickening of the adsorbed layer of gelatin around the benzene globules in Nugent's emulsions more than balances the lesser protective action of the gelatin due to ageing.

Whilst Nugent's investigation supports the theory of an adsorbed film of gelatin around the benzene globules, Holmes and Child[4] failed to determine quantitatively any adsorption of gelatin in the aqueous phase in similar emulsions. Their results, however, must be questioned, especially as Winkelbech[5] had previously visualised a film of gelatin at the dineric interface when dilute gelatin solutions and benzene were shaken together. This is to be expected, since, as Bancroft[6] points out, the less readily an emulsifier is peptised by one of the liquids, the more readily will it go to the interface. Solid

[1] Cf. Ramsden's work on albumin and other proteids, pp. 51, 54.
[2] *J. Ind.-Eng. Chem.*, **13**, 699 (1921).
[3] *Zeits. phys. Chem.*, **68**, 129 (1909).
[4] *J. Amer. Chem. Soc.*, **42**, 2049 (1920).
[5] *Zeits. angew. Chem.*, **18**, 1953 (1906).
[6] "Applied Colloid Chemistry" (1921), p. 260.

gelatin is not readily peptised by water, and not at all by benzene.

Interesting work on the adsorbed film in emulsions of the water-in-oil type has been done by Holmes and Cameron [1] who found that if several large drops of water are added to a solution of cellulose nitrate in a mixture of 1 part of amylacetate and 3 parts of benzene, tough elastic films are seen to surround the water drops very rapidly. For quantitative results, seven emulsions were made by dispersing 40 c.c. glycerol in 25 c.c. of acetone solutions of cellulose nitrate, using a mechanical shaker holding seven bottles. The emulsions were then allowed to "cream" for eighteen hours, *i.e.*, the glycerol emulsion sinks and a clear upper layer of acetone cellulose nitrate solution appears. The cellulose nitrate content of 10 c.c. of this upper layer was determined and compared with the original strength of the solution, the difference in concentration corresponding to adsorption of the cellulose nitrate. The following results were obtained :—

Emulsion.	Cellulose Nitrate in 10 c.c. of		Cellulose Nitrate Adsorbed (per 10 c.c.).
	Solution.	Separated Layer from Emulsion.	
	gr.	gr.	gr.
1	0·0058	0·0049	0·0009
2	0·0274	0·0251	0·0023
3	0·0344	0·0310	0·0034
4	0·0531	0·0493	0·0037
5	0·0988	0·0910	0·0078
6	0·1463	0·1300	0·0163
7	—	0·2168	—

The values are plotted in Fig. 8, ordinates being adsorption of cellulose nitrate in the glycerol/acetone interface, and abscissæ the concentration in the clear layer above the emulsions. Instead of the usual curve characteristic of adsorption, an abnormal curve is given. Between 0 and 4 on the curve the

[1] *J. Amer. Chem. Soc.*, **44**, 66—70 (1922).

adsorption isotherm is followed, but after this some radical change occurs. Holmes and Cameron believe that adsorption is here so rapid that precipitation or coagulation occurs at the glycerol/acetone interface.

Besides the adsorption of solutes at the liquid-liquid interfaces, finely-divided solids may also be adsorbed, the degree

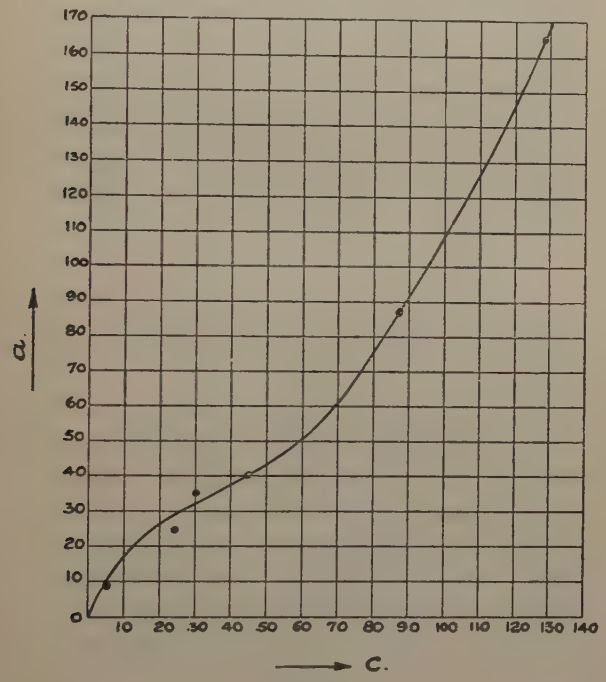


FIG. 8.

of adsorption depending essentially on the relative wetting powers of the two liquids for the solid concerned.

When a liquid impinges on a solid there is a definite angle of contact,[1] constant for a given solid and given liquid, this being the angle between the surface of the liquid and the solid-liquid interface. When a liquid wets a solid, the contact angle is zero. Another way of expressing the same result is that for wetting the difference between the surface tension of the

[1] Edser, "Flotation." *Brit. Assoc. Colloid Reports*, 4, 289 (1922).

solid and the interfacial tension at the solid-liquid boundary must be equal to or greater than the surface tension of the liquid.

Reinders [1] has discussed the distribution of finely-divided solids and colloidal suspensions between two immiscible liquids.

Let T.AS = the interfacial tension between a liquid A and the solid.

T.BS = the interfacial tension between a liquid B and the solid.

T.AB = the interfacial tension between the two liquids.

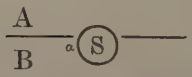
If we shake a powder of the solid with the two liquids A and B, three cases must be considered.

$$\text{(I.)}\ T_{BS} > T_{AB} + T_{AS}.$$
$$\text{(II.)}\ T_{AS} > T_{AB} + T_{BS}.$$
$$\text{(III.)}\ T_{AB} > T_{BS} + T_{AS}.$$

In the first case the solid will remain entirely in the liquid A, and in the second case entirely in the liquid B. In the third case the powder goes to the interface, tending to separate the two liquids. When none of the three tensions exceeds the sum of the other two, the powder goes to the interface and the three phases meet at a certain contact angle. These deductions readily follow the application of the Le Chatelier-Braun principle of mobile equilibrium.

All finely-divided solids which act as emulsifiers appear in the interface between the two emulsion-liquids, and their distribution is determined as follows :—

Consider a solid sphere S at the interface between the liquids A and B,



Equilibrium attains when $T_{AB} = T_{BS} + T_{AB}\cos\alpha$, where α is the angle of contact. If $T_{AS} > T_{BS}$, then $\cos\alpha$ is positive and $\alpha < 90$ degrees. The greater portion of the solid is then bathed by liquid B, *i.e.*, its equator is in liquid B. If

[1] *Koll. Zeits.*, **13**, 235 (1913) ; *vide* also Rickard, "Concentration by Flotation" (N.Y., 1921), pp. 335—340 ; Bancroft, "Applied Colloid Chemistry" (1921), p. 86.

$T_{AS} < T_{BS}$, then $\cos\alpha$ is negative, and $\alpha > 90$ degrees. The major portion of the sphere is then immersed in the liquid A.

Early work on the concentration of dissolved substances at various dineric interfaces was done by Wilson,[1] Swan,[2] von Lerch,[3] and Tomlinson.[4] Hofmann [5] investigated the concentration of small solid particles at the interface between chloroform and water, using finely-divided red lead. When this solid is shaken with chloroform and water, the chloroform droplets become coated with red lead, and so are kept emulsified in the water phase. Hofmann's explanation, following ideas expressed by Des Coudres,[6] is to the effect that, when a finely-divided solid is preferentially wetted by water more than by chloroform, the water will displace chloroform and form an aqueous film around the particles of the solid, which will tend to remain in the aqueous phase owing to the fact that work must be done to effect their removal therefrom. In the case of an organic liquid heavier than water, like chloroform, the solid particles will remain in the water, except for those whose size necessarily makes them sink under gravitational force. With a liquid such as benzene—lighter than water—the particles will all remain in the water phase.

An extension of this rule is that if the chloroform or benzene wets the solid more strongly than does water, globules of water will persist, surrounded by solid particles, and all suspended in a continuous phase of chloroform or benzene.

Recent Views on Interfacial Tension and Adsorption.—The usual view of surface tension, due to Laplace,[7] is based on the theory that the molecules in the surface of a liquid experience an inward pull of considerable magnitude due to the attraction of the molecules in the interior of the liquid. The molecules in the bulk of the liquid are attracted on all sides, whilst those at the surface are subjected to an unbalanced attraction.

[1] *J. C. S.*, **1**, 174 (1848).
[2] *Phil. Mag.*, **33**, 36 (1848).
[3] *Drude's Ann.*, **9**, 434 (1902).
[4] *Phil. Trans.*, **161**, 51 (1871).
[5] *Zeits. phys. Chem.*, **83**, 385 (1913).
[6] *Arch. Entwicklungsmechanik*, **7**, 325 (1898).
[7] *Vide* Maxwell and Rayleigh, *Enc. Brit.*, "Capillarity"; Hatschek and Willows, "Surface Tension and Surface Energy" (London, 1915); Edser, "General Physics for Students," Chaps. X. and XVI.; Hardy, *Nature*, **109**, 375 (1922).

The peculiar condition of tension at the surface of a liquid is ascribed as being due to this inward pull on the surface molecules.

Recently, Langmuir [1] and Harkins,[2] working on somewhat different lines, have independently arrived at the same conclusions regarding the *structure* of liquid surfaces and the nature of surface tension. The basic idea involved is that in the surface of a liquid in contact with air (or its own vapour) the molecules are orientated, and the main factor determining the surface tension is the structure of the surface layer of atoms. The surface molecules are so orientated that their most active portions are drawn inwards, so that the least active portions of the molecules (orientated towards the vapour phase) characterise the surface layer. The active portion of the molecule is considered to possess a strong stray field or residual valence, hence the molecules in a surface layer are packed in such a manner that this residual valence is a minimum. On this view, surface tension (or surface energy) is defined by Langmuir as " a measure of the potential energy of the electromagnetic stray field which extends out from the surface layer of atoms. The surface energy of a liquid is thus not a property of the group molecules, but depends only on the *least active portions of the molecules* and on the manner in which these are able to arrange themselves in the surface layer."

Thus in the liquid paraffin series of hydrocarbons the molecules are so arranged that the CH_3 groups at the ends of the hydrocarbon chains form the surface layer, no matter how long the chain may be. Experiment shows that the whole series, from hexane to molten paraffin, have practically the same surface energy, viz., 46 to 48 ergs/cm^2., although their molecular weights greatly vary. For organic liquids in general the active groups, such as NO_2, CN, COOH, COOM, COOR, NH_2, $NHCH_3$, NCS, COR, CHO, I, OH, are orientated towards the interior of the liquid, as also are groups which contain N, S, O, I, or double bonds. Langmuir's work on the surface films of organic liquids on water or mercury, and Harkin's

[1] Langmuir, *J. Am. Chem. Soc.*, **39**, 1848 (1917).
[2] Harkins *et al*, *J. Am. Chem. Soc.*, **39**, 354, 541 (1917).

work on surface tension phenomena strongly support the new ideas. Confirmatory experimental evidence has also been obtained by Adam [1] and Woog.[2]

For the study of emulsions the nature of the interface between two liquids is all important. Evidence has accumulated which supports the view that, when two pure liquids are in contact, their like parts orientate towards each other, the separating boundary surface thus possessing a definite packing or structure of molecules. Thus, when an organic liquid and water make an interface, the organic radical turns towards the organic liquid, and the active or "polar" group towards the water. As an example we may consider a film of oleic acid [$CH_3.(CH_2)_7.CH : CH(CH_2)_7.COOH$] spreading on water. The COOH groups "dissolve" in the water, *i.e.*, combine with the water by virtue of the secondary valences. The long hydrocarbon chain is orientated away from the water. The molecules of oleic acid arrange themselves in the surface of the water with their hydrocarbon chains packed in side by side and vertically above the COOH groups. A film of *monomolecular thickness* is thus produced. From such considerations it follows that the hydrocarbons, without active or polar groups which can combine with water, should not spread on a water surface, and experiment has definitely proved this with pure paraffin oil, which does not spread as a uniform film on water.[3]

Having accepted the view that the liquid-liquid interface possesses a definite structure, it is necessary to consider from the newer standpoint the interfacial changes occurring when an emulsifying agent becomes adsorbed at the interface.

Harkins has pointed out the general law that "at any surface or interface the change which occurs is such as to make the transition to the adjacent phase less abrupt." The orientation of molecules in a liquid-liquid interface is such as to turn like groups towards like groups. The free energy decrease, when the surface of a given liquid comes into contact with the surface of a polar liquid like water, depends essentially

[1] *Nature*, **107**, 522 (1921); *Proc. Roy. Soc.*, **99A**, 336 (1921).
[2] *Comptes rendus*, **173**, 387 (1921).
[3] Hardy, *Proc. Roy. Soc.*, **86a**, 632 (1912); Edser, *Brit. Assoc. Colloid Reports*, **4**, 301 (1922).

upon the most active or polar group present in the molecule (*e.g.*, COOH), and also upon the size and shape of the molecule. Experiments show that the presence of such active or polar groups in a liquid is intimately connected with the solubility of the liquid in water, so that liquids possessing a low interfacial tension are more or less miscible.[1] As Harkins puts it : " The solubility in water is related to the free energy decrease, which more or less perfectly measures the attraction of the active group for the water molecule."

Now the solubility of one liquid in another can be considered as the extreme case of continuously increasing the interfacial separating surface between the liquids,[2] and, as we have noted, there is then no interfacial tension. Emulsions being systems of two non-soluble liquids, it follows that the presence of active or polar radicles does not in such cases call into play sufficient residual valences. A third substance must be added, and for it to be effective it must be capable of assisting or making less abrupt the transition of one liquid to the adjacent phase. Thus for two immiscible liquids an emulsifier will be adsorbed at their interface if this substance possesses molecular groups which will orientate some to one liquid and some to the other. The emulsifier must, in a sense, act as a bridge for the two dissimilar liquids. By being adsorbed at the interface, the tension there is diminished, and diminished interfacial tension permits increased subdivision of one of the liquids in the other.[3] Thus sodium oleate decreases the free energy between benzene and water, and promotes the emulsification of benzene in water. Which of the two liquids becomes dispersed as globules in the other liquid depends on the mode of orientation and the strength of the residual valences called into play when the emulsifying agent is adsorbed at the interface.[4]

To reiterate, the essential point regarding emulsifying agents

[1] When two liquids, very dissimilar, are in contact the boundary molecules of each liquid will be orientated towards the interior of their own liquid, and a high interfacial tension (corresponding to the Laplace surface tension) may be produced. If the polar end of a molecule of liquid is orientated towards the other liquid, the interfacial tension is necessarily decreased until, with two liquids perfectly miscible, the interfacial tension becomes zero.

[2] *Vide* Mees, *Chem. Weekblad.*, **19**, 82 (1922).

[3] Cf. Wilson and Barnard, *J. Ind. Eng. Chem.* **14**, 690 (1922).

[4] *Vide* p. 97.

in general is that they are orientated at the liquid-liquid interface, and orientated in such a way as to reduce the free surface energy to a minimum. The polar or active end of the emulsifier is orientated towards the more polar or active liquid, and the less polar end towards the less polar liquid. Thermodynamically this idea is thoroughly sound.

CHAPTER V

DUAL EMULSIONS AND THE INVERSION OF PHASES

With two immiscible liquids A and B, it is theoretically possible to obtain two types of emulsion, viz., A dispersed in B, and B dispersed in A. Moreover, it would seem at first that one should be able to produce these two sets of emulsions with any given phase ratio, *e.g.*, from 1 per cent. of A in B, or B in A, up to, say, 99 per cent. A in B, or B in A.

The earlier workers on emulsions all dealt with the familiar type where oil was the dispersed phase, water or an aqueous solution being the dispersing medium. Recently it has been shown that water can be dispersed in organic media to form stable emulsions, and various investigators have realised experimentally the theoretical emulsions mentioned above. The subject has much practical application in various industries, *e.g.*, paints, butter and margarine, but its greatest importance lies in its fundamental bearing on the general theory of emulsions and emulsifications, and has, in fact, led to the present widely accepted " adsorption-film " theory of emulsions.

As we have already seen (p. 31), Ostwald [1] recognised two types of emulsions, but believed that dual emulsions were restricted within definite phase-volume relationships. He, however, pointed out the significant fact that two emulsions of the same concentration values, but of opposite types, would possess entirely different properties.

The present discussion is concerned not so much with the making of an emulsion of a given type as with the *reversal* of a given emulsion to one of the opposite type by appropriate means, excluding mechanical means.[2]

Robertson [3] was one of the first investigators in this connection, but his work was really an investigation on phase-volume

[1] *Koll. Zeits.*, **6**, 103 (1910), and **7**, 64 (1910).
[2] As in the churning of butter, or the " rolling " of margarine.
[3] *Koll. Zeits.*, **7**, 7 (1910).

relationships, and as such has already been discussed. The fact that he obtained inversion and two types of emulsion is important; his quantitative results, however, are unsatisfactory.

Newman[1] has investigated the two types of emulsion obtained with water and benzene. He found that, using sodium oleate as emulsifier, water was always the external phase, no matter what phase ratio he took. Even 99 c.c. of benzene could be emulsified in 1 c.c. of water containing about 0·05 gr. sodium oleate. This particular emulsion was a stiff jelly. When magnesium oleate was the emulsifying agent employed, Newman obtained emulsions of water in benzene. Newman found that emulsions of water in benzene stabilised by magnesium oleate could be inverted by adding sufficient sodium oleate. Similarly, emulsions of water in carbon disulphide could be inverted.

Briggs and Schmidt[2] extended this work and confirmed Newman's results. Emulsions containing over 90 per cent. of water dispersed in benzene were easily obtained when magnesium oleate was the emulsifying agent. The emulsions of water in benzene, however, are not as stable as those of benzene in water. Barium oleate was not so effective as magnesium oleate.

The first thorough study of the actual inversion of an oil-in-water emulsion to one of water-in-oil is due to Clowes, who undertook the work as a result of Bancroft's observation that sodium soaps promote the emulsification of oil in water, whilst calcium soaps promote the reverse type. Similar antagonistic effects are familiar in biology, *e.g.*, the formation of a blood clot from blood plasma, or a casein clot from a casein suspension, both of these processes, as pointed out by Clowes, being promoted by calcium salts and inhibited or retarded by alkalies and sodium salts. As far as physiological systems are concerned, the first to recognise the antagonistic effects of NaCl and $CaCl_2$ therein was Mathews,[3] whilst Clowes first appreciated

[1] *J. Phys. Chem.*, **18**, 34 (1914).
[2] *Ibid.*, **19**, 478—499 (1915).
[3] *Am. Journ. Physiol.*, XI., 455 (1904).

their influence in emulsion systems, since he showed that an emulsion of oil in water could be changed into one of water in oil by shaking with calcium salts.[1] Shaking again with a sufficient quantity of NaOH would reconvert the emulsion to its original type. Later, Clowes[2] showed that in the case of emulsions of olive oil in water, stabilised by adding NaOH, the addition of $CaCl_2$ can lead to a critical condition where the tendency towards the formation of the two types of emulsions is almost the same. This occurs when equivalent amounts of Ca and OH ions are present, the directive action of the Ca ions being counterbalanced by the action of the OH ions.

He further showed that, in the case of oil-in-water emulsions to which varying amounts of $CaCl_2$ and sodium citrate were added, the antagonistic effects of the calcium and citrate ions disappeared when the two ions were present in the ratio of 1 : 2. A solution of $CaCl_2$ and sodium citrate, in which the ratio of Ca ion to citrate ion is 1 : 2, exerts no influence on the hæmolysis of blood corpuscles, and is inactive when injected intravenously into mice. Solutions where this ion ratio is departed from at once produce positive effects. Clowes tentatively suggested that the activity of the ions was resultant upon adsorption.

Osterhout[3] and Loeb[4] have repeatedly demonstrated most interesting antagonistic effects of electrolytes in biological processes, and investigated them quantitatively.

In an exhaustive paper entitled "Protoplasmic Equilibrium" Clowes,[5] in 1916, gave a detailed discussion on the inversion of emulsions. At the onset he made it clear that in the inverting action of $CaCl_2$ on emulsions of oil in very dilute NaOH there is no antagonistic action between the cations Ca and Na, but rather between cations and anions adsorbed on or reacting with the surface films or enveloping membranes which surround the dispersed globules in a stable emulsion. "It simply happens that, in the case of $CaCl_2$, the cation Ca is far more

[1] *Proc. Soc. Exp. Biol. and Med.*, XI., 1 (1913).
[2] *Koll. Zeits.*, **15**, 123—126 (1914).
[3] *Plant World*, **16**, 129 (1913); *J. Biol. Chem.*, **19**, 335 (1914); *Science*, **41**, 255 (1915).
[4] "Artificial Parthenogenesis and Fertilisation" (1913); "The Mechanistic Conception of Life" (1912).
[5] *J. Phys. Chem.*, **20**, 407—451 (1916).

readily adsorbed than the anion Cl, while in the case of NaCl the anion Cl is somewhat more readily adsorbed than the cation Na."

The emulsions contained equal volumes of water and olive oil, the latter containing sufficient free oleic acid to form soap with all the added NaOH. Shaking was carried out by a mechanical shaker, followed by hand shaking. The effect of varying proportions of NaOH and $CaCl_2$ on such an emulsion containing 10 c.c. each of oil and water is shown in the following table :—

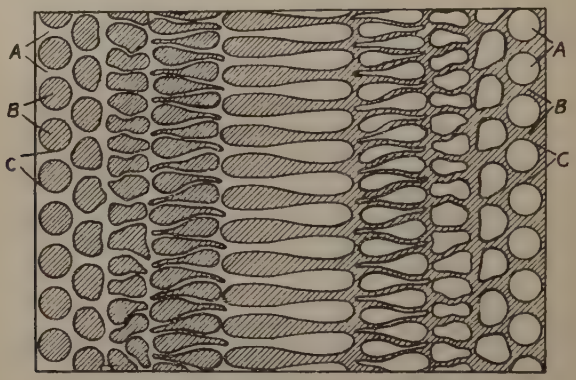
Vol. of M/10 NaOH employed. (cc.)	Vol. of M/10 $CaCl_2$ employed. (cc.)			
	0·25	0·5	0·75	1·0
1	R	W — O	W — O	W — O
2	O — W	R	W — O	W — O
3	O — W	O — W	R	W — O
4	O — W	O — W	O — W	R

W — O = water-in-oil emulsion.
O — W = oil-in-water emulsion.
R = critical (inversion) point.

These results show that, when the ratio of NaOH to $CaCl_2$ is exactly 4 : 1, neither type of emulsion predominates. Oil-in-water emulsions result when this ratio is greater than 4 : 1, and water-in-oil emulsions when the ratio is less than 4 : 1. At the critical point one chemical equivalent of $CaCl_2$ is always present with two of NaOH, so that sodium oleate and calcium oleate are present in equivalent proportions. The type of emulsion, therefore, depends on the nature of the soap present, sodium oleate leading to dispersion of oil in water, and calcium oleate to dispersion of water in oil. The theoretical explanation of this has been advanced by Bancroft and accepted by Clowes, and is dealt with in the following chapter.

Clowes followed the actual inversion of an oil-in-water emulsion by means of the microscope. The oil globules become distorted,

and near the critical point become elongated. At this stage the Brownian movement is very prominent. At the critical point large masses of oil and water are in very active movement, probably owing to the existence of two continuous phases. When the critical point is passed, the emulsion mainly contains large drops of water surrounded by oil. In the water drops there are still small globules of oil exhibiting rapid Brownian movement ; conversion to the water-in-oil emulsion is regarded as complete when this particular Brownian movement entirely ceases. A schematic presentation of such inversion is given by Clowes, and reproduced in Fig. 9.



A = water ; B = oil ; C = adsorbed film.
Fig. 9.

Parsons and Wilson [1] have also described the behaviour of emulsions when undergoing inversion. Using emulsions of "Nujol" (mineral oil) in dilute sodium oleate solutions and adding magnesium salts, inversion was obtained. The first effect of adding a Mg salt was greatly to lower the viscosity of the oil-in-water emulsion. This was followed by an increase in viscosity, with oil appearing as the external phase. The explanation advanced for these effects is that the Mg salt reacted with the sodium soap in the adsorbed film, and caused a temporary breaking of the emulsion. The magnesium oleate produced by metathesis then dissolved in the oil, promoting an emulsion of water in oil, a system of the viscosity characteristic of emulsions.

[1] *J. Ind.-Eng. Chem.*, **13**, 1119 (1921).

Other electrolytes were investigated, and it was found that salts of Mg, Sr, Ba, Fe, Al, etc., exerted a comparable effect to Ca, whilst in place of NaOH could be used KOH, LiOH, etc. With $MgCl_2$ and NaOH a critical ratio appears when the proportions of Na oleate and Mg oleate are equivalent. Clowes classified electrolytes into two main groups: (1) promoting dispersion of oil-in-water—salts of the monovalent cations Li, Na, K, etc., alkalies, salts of di- and trivalent anions; (2) promoting dispersion of water-in-oil—salts of the di- and trivalent cations Ca, Sr, Ba, Fe, Al.

Employing a Traube stalagmometer, Clowes determined the number of drops obtained when a given volume of solutions of electrolytes was run into olive oil containing "a certain amount of oleic acid." The principle involved is that underlying the Donnan pipette, namely, that the greater the number of drops obtained the more pronounced is the tendency to produce emulsification.

Clowes found that NaCl and KCl in small amounts promoted the formation of emulsions of oil-in-water, and counteracted the effect of $CaCl_2$ in the approximate ratios of 100 to 150 molecules of NaCl to one of $CaCl_2$. Apparently this is due to an adsorption of Cl ions in excess of Na ions on the soap film, or to an increased adsorption of OH ions already present in the system. The following table of drop numbers is given by Clowes, and shows the opposing influences of NaCl and $CaCl_2$:—

Experiment.	Concentration of			Drop number.	Mol. ratio NaCl : $CaCl_2$.
	NaOH.	NaCl.	$CaCl_2$.		
1	0·001 M	—	—	44	—
2	,,	0·15 M	—	300	—
3	,,	—	0·0015 M	24	—
4	,,	0·15 M	0·0015 M	44	100 : 1
5	,,	0·3 M	0·003 M	43	100 : 1
6	,,	0·45 M	0·005 M	43	100 : 1·1
7	,,	0·6 M	0·01 M	43	100 : 1·6

The dispersing influence of NaCl is well illustrated in experiment 2, and the opposite effect of $CaCl_2$ in experiment 3.

When the NaCl and $CaCl_2$ are in such amounts as to correspond to the ratio of about 100 molecules NaCl to one molecule of $CaCl_2$, the drop number attains the same value as the original number obtained with NaOH alone, thus showing that the opposing effects of NaCl and $CaCl_2$ are counterbalanced. This ratio of 100 : 1 also appears to be the balancing ratio in certain biological systems, as demonstrated by Loeb.

Clowes argues that the antagonistic effects of various electrolytes on emulsions and biological systems may be used to classify electrolytes into two main groups : (1) those possessing a relatively more readily adsorbed or reactive cation than anion, and (2) those possessing a relatively more readily adsorbed or reactive anion than cation. "Balanced solutions are those in which the relative proportions of cations and anions reacting with or adsorbed by colloidal constituents of the surface film are such that no change occurs in the charge in the state of dispersion, and consequently in the permeability of the film."

Clowes summarises his own work in the statement that emulsion equilibrium depends on the relative proportion of positive and negative ions adsorbed by the stabilising film around the dispersed globules ; when negative ions are in excess, the oil-in-water type of emulsion is favoured, whilst an excess of positive ions has the reverse effect. This idea has been favoured by Bhatnagar,[1] who, however, has pointed out its limitations and shown how it should be extended.

The idea that adsorption of ions is the underlying factor in emulsion equilibrium is supported by experiments of Clowes wherein he shows that the ratio between the number of drops obtained when varying concentrations of sodium oleate solutions flow into oil, and the concentration of the soap is always logarithmic.[2] Also, when electrolytes like NaOH or $CaCl_2$ are added, the ratio between the number of drops and the concentration of the electrolyte is again logarithmic. In support of this, too, is the fact that a logarithmic relationship holds for the ratio of concentration of added NaCl, and the concentration of the OH ions in the aqueous phase, when NaCl is added to an emulsion of oil in water.

[1] See p. 97.
[2] See p. 59.

Bhatnagar has made considerable investigation into the inversion of emulsions by electrolytes, employing the electrical method suggested by Clayton [1] as a sensitive means of detecting the inversion point. His first experiments [2] were with emulsions of paraffin oil (B.P.) and water in equal volumes, the oil containing 1 per cent. of oleic, stearic, or linoleic acid. The oil was shaken in a mechanical shaker with the water, to which varying proportions of KOH and electrolytes had previously been added. The reversing effect of barium nitrate on an emulsion of paraffin oil containing 1 per cent. oleic acid and varying amounts of KOH is shown in the following table. The volume of oil was 10 c.c., and the volume of the aqueous phase was maintained throughout at 10 c.c. :—

Vol. M/50 KOH c.c.	Vol. M/50 $Ba(NO_3)_2$ c.c.						
	0·2	0·4	0·6	0·8	1·0	1·2	1·4
1	R	W—O	W—O	W—O	W—O	W—O	W—O
2	O—W	R	W—O	W—O	W—O	W—O	W—O
3	O—W	O—W	R	W—O	W—O	W—O	W—O
4	O—W	O—W	O—W	R	W—O	W—O	W—O
5	O—W	O—W	O—W	O—W	R	W—O	W—O
6	O—W	O—W	O—W	O—W	O—W	R	W—O

The result with another strength of $Ba(NO_3)_2$ and KOH is as follows :—

Vol. M/10 KOH c.c.	Vol. M/10 $Ba(NO_3)_2$ cc.							
	0·1	0·25	0·3	0·4	0·6	0·8	1·0	1·5
1	O—W	R	W—O	W—O	W—O	W—O	W—O	W—O
2	O—W	O—W	O—W	O—W	O—W	O—W	O—W	W—O
3	O—W	O—W	O—W	O—W	O—W	R	W—O	W—O
4	O—W	O—W	O—W	O—W	O—W	?	?	?
5	O—W	O—W	O—W	O—W	O—W	O—W	O—W	W—O
6	O—W	O—W	O—W	O—W	O—W	O—W	O—W	R

[1] *Brit. Assocn. Colloid Reports*, **2**, 114 (1918).
[2] Bhatnagar, *J. C. S.*, **117**, 549—552 (1920); *vide* criticism by Bancroft, *J. Ind-Eng. Chem.*, **13**, 348 (1921).

Just as Clowes found the critical point with emulsions of oil and water containing NaOH and $CaCl_2$ was 4 molecules of NaOH to 1 molecule of $CaCl_2$, so Bhatnagar found that at the critical point the ratio of KOH to $Ba(NO_3)_2$ was 4 : 1 in concentrations ranging from M/10 KOH upwards. In lower concentrations the ratio increases; thus at M/50 KOH it is about 5 : 1. He also found that the nature of the acid in the oil influenced the critical ratio. Thus, when using KOH and $Ba(NO_3)_2$ in M/10 concentration, but replacing oleic acid with linoleic acid, the critical point was reached when the ratio of KOH to $Ba(NO_3)_2$ was 2 : 1.

Bhatnagar,[1] recognising that the presence of free alkali and free fatty acid makes the system more complex, investigated the inversion of paraffin oil (B.P.) emulsions stabilised by various *soaps*. The emulsions were made up as before, and in all cases contained 10 c.c. each of oil and the aqueous phase. Each emulsion contained a known amount of a definite soap and known quantities of various electrolytes. The results are given in the following table, and are expressed in millimols per cent. of the electrolytes at the critical (inversion) point.[2]

Emulsifying Agent.	Amount of Soap in Millimols per cent.	Electrolytes in Millimols per cent. at Inversion Point.					
		$Ba(NO_3)_2$.	$Sr(NO_3)_2$.	$Pb(NO_3)_2$.	$Ni(NO_3)_2$.	$Al_2(SO_4)_3$.	$Cr_2(SO_4)_3$.
Na. Oleate .	0·080	0·0398	0·0398	0·0396	0·036	0·014	0·016
	0·101	0·0500	0·052	0·504	0·040	0·017	0·019
	0·150	0·080	0·084	0·082	0·060	0·025	0·027
	0·162	0·084	0·090	0·088	0·076	0·027	0·030
	0·210	0·112	0·116	0·110	0·0798	0·036	0·039
K. Stearate .	0·086	0·044	0·046	0·040	0·040	0·018	0·018
	0·10	0·0508	0·0512	0·050	0·052	0·026	0·022
	0·15	0·084	0·086	0·078	0·088	0·027	0·026
	0·25	0·132	0·136	0·128	0·140	0·048	0·048
	0·30	0·156	0·160	0·150	0·154	0·056	0·057
Li. Stearate .	0·09	0·040	0·040	0·036	0·042	0·015	0·016
	0·12	0·058	0·058	0·050	0·056	0·021	0·023
	0·16	0·090	0·094	0·080	0·094	0·028	0·029
	0·20	0·102	0·104	0·096	0·106	0·03	0·032
Na. Linoleate.	0·083	0·068	0·068	0·058	0·072	0·028	0·028
	0·112	0·100	0·106	0·090	0·116	0·038	0·037
	0·125	0·128	0·134	0·120	0·136	0·042	0·043
	0·18	0·198	0·200	0·178	0·200	0·061	0·063

[1] *J. C. S.*, **119**, 61—68 (1921).

[2] *Loc. cit.*, p. 63, where "respective salts in millimols at R" should read "respective salts and soaps in millimols per cent. at R."

A study of the above results brings out several well-marked features. (*a*) There is a distinct valency effect of the electrolyte. Tervalent electrolytes, the sulphates of aluminium and chromium, are required in much smaller amounts to effect inversion of the oil-in-water emulsions than are the bivalent electrolytes. (*b*) The inverting capacity of the electrolytes follows the order $Al > Cr > Ni > Pb > Ba > Sr$ (calcium, bivalent iron and magnesium possess the same values as strontium). (*c*) The nature of the soap present influences the amounts of electrolytes required to effect the reversal of phases, but the valency effect of the electrolyte still appears.

Bhatnagar[1] observed the effect of altering the volume ratio of the phases in emulsions with different soaps and the same series of multivalent electrolytes. In all cases it was found that the amount of electrolyte necessary to effect the reversal of phases increased as the volume of the aqueous phase was increased, and diminished as it was reduced. A corresponding increase in the oil phase had the opposite effect. Thus in one case where barium nitrate was added to an emulsion of oil and water containing lithium stearate, and in which the total volume of emulsion was kept at 20 c.c., the following results were obtained :—

Ratio $\frac{\text{Vol. of Aqueous Phase}}{\text{Vol. of Oil Phase}}$.	Ratio $\frac{\text{Moles of Lithium Stearate at R}}{\text{Moles of Barium Nitrate at R}}$.
1·00	4·13
3·00	3·43
0·33	6·00

The effect of free fatty acids and alkalies on emulsion equilibrium has been found by Bhatnagar to result in a shift of the inversion point. Three sets of emulsions of the same sodium oleate content, viz., 0·162 millimols per cent., and of the same volume ratio were taken. In one the oil contained free fatty acid, in the second free alkali was present in the aqueous phase, whilst the third contained neutral oil and the

[1] *Loc. cit.*, p. 64.

soap solution. Barium nitrate was the electrolyte used, and the data given below expresses the concentration of $Ba(NO_3)_2$ at the inversion point :—

Vol. Emulsion.	Free KOH.	Free Fatty Acid.	$Ba(NO_3)_2$.
c.c.	gr.	gr.	Millimols per cent.
20	0·01	*Nil.*	0·09
20	0·021	*Nil.*	0·096
20	*Nil.*	0·003	0·078
20	*Nil.*	0·008	0·070
20	*Nil.*	*Nil.*	0·084

Apparently, free fatty acids and free alkalis shift the inversion point in opposite directions.

Parsons and Wilson [1] have studied the inversion of oil-in-water emulsions, using the highly-purified mineral oil known as "Nujol." The emulsions were passed five times through a Briggs homogeniser,[2] and the oil phase and water phase were of equal volume. The effect of the presence of opposing emulsifying agents was investigated, sodium oleate being dissolved in the water phase and magnesium oleate in the "Nujol." Numerous emulsions were made, varying the ratio of equivalent concentration of magnesium oleate to sodium oleate from 25 to 0·54. The existence of real equilibrium in the presence of these opposing emulsifiers was looked for, as well as the existence of a possible critical ratio of the reagents at which no emulsion at all would result. The general results of the work showed that a pure mineral oil behaves differently to an oil such as olive oil (as used by Clowes), since no critical ratio of magnesium oleate to sodium oleate was observed, at which inversion to a new stable emulsion would occur. Some sort of pseudo-equilibrium was reached whereby *both* types of emulsion would co-exist. This is an important point, and is stated to be under more detailed investigation.

Parsons and Wilson tried the inverting effects of various

[1] *J. Ind. Eng. Chem.*, **13**, 1116—23 (1921).
[2] *J. Phys. Chem.*, **19**, 223 (1915).

di- and trivalent salts on Nujol-in-water emulsions stabilised with sodium oleate. Aqueous solutions of $MgSO_4$, $MgCl_2$, $FeSO_4$, $Al_2(SO_4)_3$ and $FeCl_3$ were used. The volume ratio of oil to total emulsion in the resulting mixture was maintained at 0·5.

With the magnesium salts no absolutely sharp inversion point was found, but, rather, a time period of instability during which inversion took place. When the equivalent concentration of magnesium exceeded that of sodium, the original oil-in-water emulsion was completely inverted to one of water-in-oil. Both types of emulsion resulted when the equivalent concentration of magnesium approached, but did not exceed, that of sodium. It was found that the determining factor in the inversion of emulsions was the ratio of *equivalents* of magnesium to sodium, not the absolute concentrations. Variation in the *anion* of the added electrolyte had but little effect on the emulsion equilibrium.

When ferrous sulphate solution was added to Nujol-in-water emulsions, inversion occurred when the ratio of the equivalent concentration of ferrous sulphate to sodium oleate exceeded 1. The new emulsion soon broke down, since the iron soap possesses a weak emulsifying tendency.

No quantitative results are given for the effects of the trivalent electrolytes. Complete inversions took place, but the water-in-oil emulsions were very unstable, pointing to the very weak emulsifying tendencies of the aluminium and iron soaps.

Bhatnagar [1] has published a valuable paper on the reversal of emulsion type by electrolytes. These emulsions, too, were of a mineral oil (B.P. paraffin oil), but the emulsifying agents were insoluble suspensions specially prepared and purified, viz., zinc hydroxide, lead oxide, lead carbonate, casein, lecithin, egg-albumin, and rosin. The zinc hydroxide was obtained by adding KOH to a 3 per cent. solution of pure $ZnSO_4$ until the precipitated hydroxide redissolved. Dilute HCl was then cautiously added until the precipitate just reappeared. The coagulum and liquor were dialysed in parchment for five days, when the diffusion of alkali ceased and a wash-liquid neutral to

[1] *J. C. S.*, **119**, 1760—69 (1921).

litmus resulted. The coagulum was then made up to 1 litre. It was capable of maintaining stable emulsions of paraffin oil and water, the alkali-free suspensions of zinc hydroxide promoting the water-in-oil type of emulsion, whilst alkaline suspensions of zinc hydroxide promoted the reverse type. Dried zinc hydroxide was not able to stabilise emulsions at all. This may be due to the film of adsorbed air which prevents the wetting of dried powders.[1]

Several samples of zinc hydroxide suspension [2] of equal volume (20 c.c.) and weight were emulsified with 20 c.c. of oil, and the effect of various electrolytes at 17° to 19° C. investigated. The following table shows the nature of the results obtained :—

Electrolyte.		Quantity in gram-mols. per cent.	Type of Emulsion.
KCl	1	0·0005	W in O, stable.
	2	0·001	,, ,,
	3	0·005	,, ,,
K_2SO_4	1	0·0005	,, ,,
	2	0·001	,,
	3	0·006	,,
$Al_2(SO_4)_3$	1	0·0001	,,
	2	0·001	,,
	3	0·005	,,
K_3PO_4	1	0·001	,,
	2	0·002	Separation into layers.
	3	0·003	O in W.
KOH	1	0·001	W in O.
	2	0·0015	O in W.
	3	0·002	,,
NaOH		0·002	,,

Lead oxide emulsifier was prepared by the interaction of KOH and $Pb(NO_3)_2$ and dialysing the coagulum. The suspension contained 4·2 grs. lead oxide per litre. Aluminium hydroxide was obtained by treating a solution of pure $Al_2(SO_4)_3$

[1] Cf. Ehrenberg and Schultze, *Koll. Zeits.*, **15**, 183 (1914).
[2] Concentration = 3·2 grams per litre.

with $NH_4.OH$ and dialysing until the internal and external liquids were neutral to litmus. This suspension contained 3·8 grs. per litre. Casein emulsifier was prepared by dissolving a weighed quantity of pure casein in 0·1 n. KOH and gradually precipitating with acetic acid. The dialysed suspension was diluted to a concentration of 1·985 grs. per litre. The rosin emulsifier was a 0·3 per cent. solution in alcohol. The following results were obtained by adding electrolytes to emulsions stabilised with the foregoing coagula.

(*a*) Lead Oxide.—The emulsions containing 15 c.c. each of the oil, and aqueous phases were stable and of the water-in-oil type in the presence of various amounts of KCl, K_2SO_4, and $Al_2(SO_4)_3$, except when the concentration of KCl reached 0·005 gram-mols per cent., where the stability was poor. With K_3PO_4 and KOH inversion occurred. Thus :—

Electrolyte.		Quantity in gram-mols per cent.	Type.
K_3PO_4	*a* . .	0·0021	W in O, stable.
	b . .	0·008	O in W ,,
	c . .	0·009	O in W ,,
KOH	*a* . .	0·002	W in O ,,
	b . .	0·004	O in W ,,
	c . .	0·005	O in W ,,

(*b*) Aluminium Hydroxide.—The emulsions contained 20 c.c. each of the oil and aqueous phases, and were of the oil-in-water type. No inversion occurred with the addition of KCl or K_2SO_4, but the stability of the emulsions was poorer. The results with K_3PO_4 and KOH are shown in the Table on page 88.

(*c*) Casein.—The emulsions contained 20 c.c. each of oil and aqueous phase, and were initially of the oil-in-water type. Addition of KCl, K_2SO_4, $Ba(NO_3)_2$ and K_3PO_4 caused no inversion and had practically no effect on the stability of the emulsions. Inversion was obtained with $Al_2(SO_4)_3$ at a concentration of 0·003 gram-mols per cent., with $Th(NO_3)_4$ at

Electrolyte.		Quantity in gram-mols per cent.	Type.	Stability.
KP_3O_4	*a*	0·001	W in O	Not very stable.
	b	0·0035	—	Tendency to separate into two layers.
	c	0·004	O in W	Stable.
KOH	*a*	0·001	—	Tendency to separate into two layers.
	b	0·0015	O in W	Stable.
	c	0·002	O in W	Stable.

a concentration of 0·00035 gram-mols per cent., and with HCl at a concentration of 0·004 gram-mols per cent.

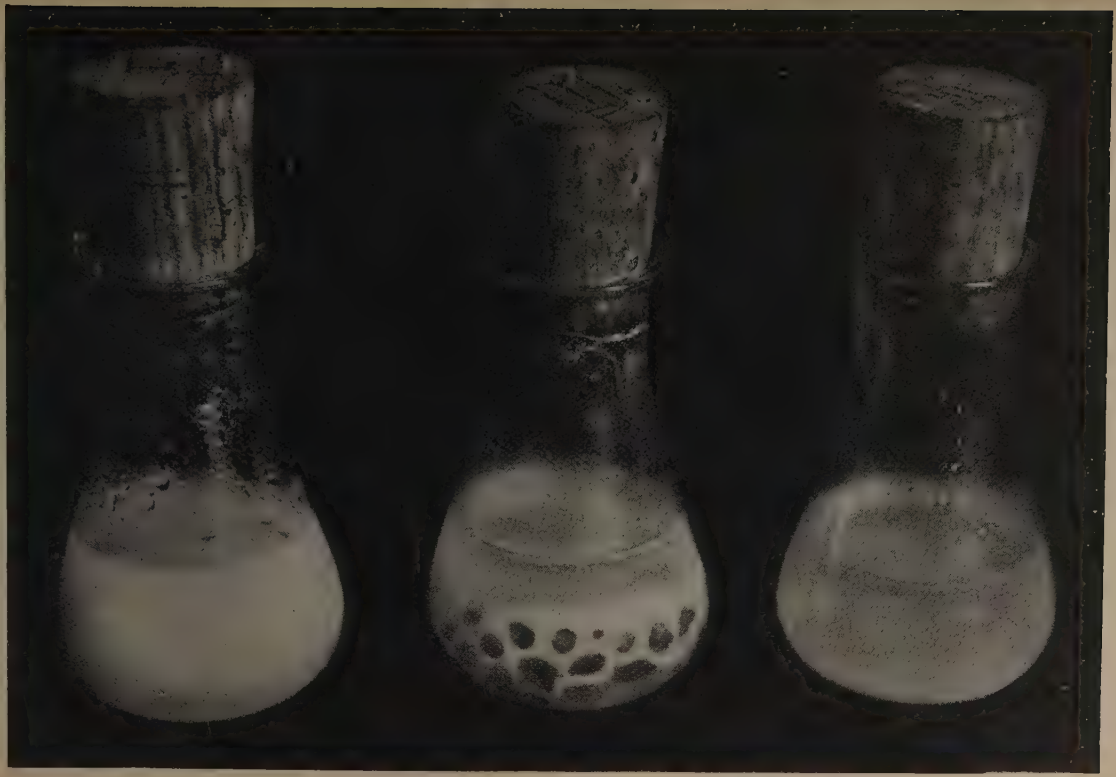
(*d*) Rosin.—The emulsions, initially of the water-in-oil type and quite stable, contained 20 c.c. each of the oil and aqueous phases. Inversion was not effected by adding KCl or K_2SO_4. With KOH at a concentration of 0·002 gram-mols per cent. inversion to a stable oil-in-water emulsion occurs. K_3PO_4 is also capable of inverting the water-in-oil emulsion.

In the discussion of his results Bhatnagar mentions that lecithin and egg-albumin promote the oil-in-water type of emulsions. The addition of a small quantity of KOH, K_3PO_4 or Na_2CO_3 to the aqueous phase increases the stability of such emulsions, whilst addition of sufficient acid inverts the emulsions to the unstable water-in-oil type. A zone of instability precedes the inversion, and this zone is clearly seen in most cases, especially when sufficient emulsifying agent is present. Fig. 10 illustrates the opposite emulsions and the zone of instability when PbO is the emulsifier and KOH the reversing electrolyte.

Bhatnagar formulates two empirical rules which hold for his results: (1) "An emulsion of water in oil can be transformed into one of oil in water by electrolytes having reactive anions like OH' and PO_4'''. (2) An emulsion of oil in water can be transformed into the reverse type by electrolytes having reactive cations like $H\cdot$, $Al\cdot\cdot\cdot$, $Fe\cdot\cdot\cdot$, and $Th\cdot\cdot\cdot\cdot$."

Clowes[1] deduced a similar classification of what he termed

[1] *J. Phys. Chem.*, **20**, 449 (1915).



Oil-in-Water Emulsion. Zone of Instability. Water-in-Oil Emulsion.

FIG. 10.

To face p. 88.

"antagonistic electrolytes" into two groups: "The first consists of di- and trivalent cations, etc., which possess a more readily adsorbed cation and promote the formation of the emulsion of water in oil; the second consists of alkalies, salts of monovalent cations, and of di- and trivalent anions which possess a more reactive and more readily adsorbed anion, and appear to exert the reverse effect of promoting the formation of oil dispersed in water."

Summarising his own work, Bhatnagar gives the following table dealing with emulsion reversal :—

Emulsifying Agent.	Reversing Electrolyte. Salts of :—	Emulsion Type.	Adsorbed Ions. Excess of :—
Sodium oleate .	Ba, Ca, Sr, Fe, Cr . .	O in W	+ ions.
	Al, Cu, Zn, Ni . . .	O in W	+ ,,
Carbon . .	KOH, K_3PO_4 . . .	W in O	— ,,
Casein . .	Al, Fe, Th, H . . .	O in W	+ ,,
Albumin . .	——	—	+ ,,
$Zn(OH)_2$ neutral	KOH, K_3PO_4 . . .	W in O	— ,,
$Zn(OH)_2$ alkaline	Al, Th, H	O in W	+ ,,
$Al(OH)_3$ . .	KOH, K_3PO_4 . . .	W in O	— ,,
PbO . .	KOH	W in O	— ,,
Rosin . .	KOH, K_3PO_4 . . .	W in O	— ,,
Lecithin . .	Al, Fe, Th	O in W	+ ,,
Univalent soaps.	Bivalent and tervalent metals	O in W	+ ,,

CHAPTER VI

THE MODERN ADSORPTION FILM THEORY

We have seen that emulsions of oil in water or of water in oil may be prepared by suitably choosing the emulsifying agent, which is invariably necessary in order to obtain emulsions of even moderate concentration of the dispersed phase. Such emulsions may also be inverted to systems of the opposite type by adding suitable electrolytes. Any general theory of emulsions and their stability may be capable of including and explaining all the above facts. The present widely-accepted theory of emulsions, postulating an adsorbed film or membrane around the dispersed globules, has been developed from Donnan's earlier work on the interfacial tension in emulsions, as discussed in Chapter III.

Bancroft,[1] in 1913, deduced the underlying principles of the modern theory. He accepted Donnan's surface tension theory, but pointed out its limitations, the chief of which was that Donnan only formulated the conditions for the formation and stability of oil-in-water emulsions; *two* emulsion types were not considered. Donnan's idea that, in the case of soap emulsions, the gelatinous soap film around the oil globules is part of the water phase, but differing in concentration, was replaced by considering this film as a *separate* phase separating the oil and water phases. On the relative magnitudes of the surface tensions on each side of this film depend the type of emulsion promoted. Both the oil and the water phase are considered to wet the film and to be adsorbed by it, so that, in general, there will exist a difference in the surface tensions on the two sides. Due to this difference, the film will bend, the side with the higher surface tension becoming concave, consequently tending to envelop liquid on that side. Thus, theoreti-

[1] *J. Phys. Chem.*, **17**, 514—18 (1913).

cally, a liquid A will be dispersed as drops in a liquid B when the interfacial tension between B and the film is less than the interfacial tension between A and the film.

On the nature of the emulsifying agent depends the type of emulsion produced. The coherency and permanency of the film formed are determining factors in the stability of the emulsion. As a corollary to this, Bancroft formulated that "a hydrophile colloid will tend to make water the dispersing phase, while a hydrophobe colloid will tend to make water the dispersed phase."

In a later paper Bancroft [1] extended his theory and pointed out that, for a substance to act as an emulsifying agent, it must necessarily be adsorbed into the surface separating the two liquids and form a coherent film there. If it was not so adsorbed into the dineric interface it would be unable to form a film enveloping globules of one of the liquids.

Extending the theory to finely-divided solids as emulsifiers, the work of Des Coudres and Hofmann leads to the conclusion that, for a solid to remain in the water phase, it must be wetted only by water; for it to remain in the non-aqueous liquid, it must be wetted only by that liquid. It will remain in the interface between the two liquids when it is partially wetted by each. Bancroft [2] prefers an alternative explanation, viz., "When shaken with water and a non-miscible organic liquid, solid particles tend to go into the water phase if they adsorb water to the practical exclusion of the other liquid; they tend to go into the other liquid phase if they adsorb the organic liquid to the practical exclusion of the water; and they tend to pass into the dineric interface in case they adsorb the two liquids simultaneously."

Clowes [3] has submitted Bancroft's ideas to experimental investigation, and has published important work on emulsion reversals which makes possible a fairly definite formulation of the theory of emulsion type and stability. At the outset he pointed out that the production of even a temporary emulsion

[1] *J. Phys. Chem.*, **19**, 275 (1915).
[2] *Loc. cit.*, pp. 287 and 308.
[3] *J. Phys. Chem.*, **20**, 407—451 (1916).

with more than a very small disperse-phase concentration appears to depend on the presence in the system of a third substance which can be adsorbed at the dineric interface and form a protecting film around the dispersed globules, oil or water, as the case may be.[1] The dispersing and the stabilising effects of this film may be due in various measures to (*a*) the lowering of the interfacial tension between the two phases, tending to oppose coalescence of the globules ; (*b*) the conferring of an electric charge on the dispersed phase, electrical repulsion opposing coalescence ; (*c*) a mechanical action aiding in keeping the particles apart. Such films have been visualised by Clowes and other workers.[2]

Clowes re-worded Bancroft's theory concerning this film formation and the type of emulsion produced. Considering the system oil and soap solution : "The soaps tend to concentrate at the interface between oil and water and to form a coherent film. Soaps of monovalent cations, being readily dispersed in water, but not in oil, form a film or diaphragm which is wetted more readily by water than by oil ; consequently the surface tension is lower on the water side than on the oil side. Since the area of the inside face of a film surrounding a sphere is smaller than that of the outside face, the film tends to curve so that it encloses globules of oil in water, in this manner reducing the area of the side of higher surface tension to a minimum as compared with that of lower surface tension. On the other hand, a film composed of soaps of di- or trivalent cations, being freely dispersed in oil, but not in water, is wetted

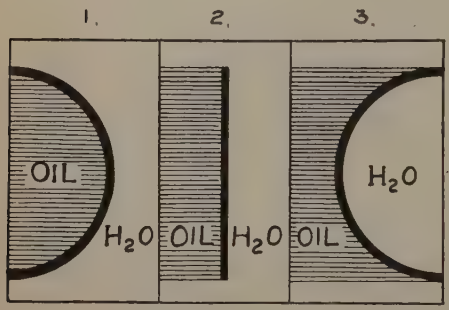


Fig. 11.

[1] Cf. Holmes and Cameron, *J. Amer. Chem. Soc.* **44**, 70 (1922).

[2] Ramsden, *Proc. Roy. Soc.*, **72**, 156 (1903) ; Briggs and Schmidt, *J. Phys. Chem.*, **19**, 496 (1915) ; Holmes and Cameron, *J. Amer. Chem. Soc.*, **44**, 66 (1922) ; Clark and Mann, *J. Biol. Chem.*, **52**, 157 (1922).

more readily by the oil than by the water. The surface tension is lower on the oil than on the water side, and the film tends to curve in such a manner as to enclose the globules of water in an outer or continuous oil phase." This is schematically represented by Clowes as in Fig. 11.

When opposing emulsifying agents are present in the system to an extent that their effects are counterbalancing, the film does not curve in either direction, so that, when agitation ceases, the two phases readily settle out under gravitational influence. In other words, the surface tension on each side of the film is the same.

As we have already seen, Clowes studied the opposing influences of $CaCl_2$ and NaOH on olive oil emulsions. He found that salts of Mg, Sr, Ba, Fe, Al, etc., behaved similarly to Ca salts, whilst KOH, LiOH, etc., could be used instead of NaOH. The effects of NaCl were very interesting, inasmuch as small amounts promoted the formation of oil-in-water emulsions. Similar effects have been observed in other emulsions by Clayton,[1] Ayres,[2] and Herschel,[3] but Briggs [4] finds no evidence for the emulsion-promoting properties of NaCl with benzene. His results are supported by the work of Harkins and Humphery,[5] who found that NaCl increases the interfacial tension between water and benzene. Clowes advanced the view that NaCl assists the emulsification of olive oil in dilute soap solutions, because there is an adsorption of Cl ions in excess of Na ions on the soap particles, or to an increased adsorption of OH ions already present in the system. In support of this it can be showns that emulsion of oil in water, to which enough NaOH has been added to render them very pink to phenol-phthalein, may then be decolorised by adding moderate amounts of NaCl. It was further found that, if NaCl be added to emulsions of olive oil in dilute NaOH and then HCl was added to a common colour standard (using phenol-phthalein as indicator), the amount of HCl required exhibited

[1] "Margarine" (Longmans, 1920), p. 72.
[2] *Chem. Met. Eng.*, **22**, 1061 (1920).
[3] U.S. Bur. Standards, Tech. Papers No. **86**, 17 (1917).
[4] *J. Ind. Eng. Chem.*, **13**, 1009 (1921).
[5] *J. Am. Chem. Soc.*, **38**, 242 (1916).

an approximately logarithmic relation to the amount of NaCl added,[1] the maximum amount being required for the control emulsion without NaCl and the minimum for that containing NaCl at a concentration of 0·1 M. Conducting the same tests, but without oil present, gave similar results, indicating that the effect is exerted on the soap particles themselves. The general conclusion, then, is that "the addition of NaCl to the emulsion system up to a concentration of 0·1 M. promotes the adsorption of negative ions on the soap particles, and consequently promotes the dispersion of soap in water, thus facilitating the formation of emulsions of oil dispersed in water."

With higher concentrations of NaCl (0·35 M. to 0·4 M.) the stabilising soap film is precipitated and the emulsion breaks.[2]

Clowes determined the drop numbers [3] of NaOH and $Ca(OH)_2$ solutions when flowing into olive oil, in order to study the effects of ions on the interfacial soap films. The following table shows the number of drops given by different strengths of NaOH and $Ca(OH)_2$:—

NaOH.	Number of Drops.	$Ca(OH)_2$.	Number of Drops.
0·0005 N	22	0·01 N	30
0·0006 N	26	0·02 N	29
0·0008 N	33	0·03 N	47
0·001 N	39	0·032 N	53
0·0012 N	50	0·036 N	73
0·0014 N	79	0·04 N	Chain.
0·0016 N	About 120.	—	—
0·002 N	Chain.	—	—

The results (excluding the unreliable upper and lower ones) indicate an approximately logarithmic relation between the concentration of alkali and the drop number, supporting the view that adsorption and surface film phenomena are involved.

[1] *Vide* logarithmic adsorption equation, p. 59.
[2] See p. 133.
[3] See p. 101.

Increase in the drop number of NaOH in oil means a greater lowering of interfacial tension and greater dispersion of oil; in other words, the relative permeability of the system to water is increased. When the drop number becomes so great that the alkali solution streams through the oil, the system is freely permeable to water, *i.e.*, an emulsion of oil in water is established with ease. Similarly, when on the addition of a calcium salt to the system oil-water-caustic soda, the drop numbers progressively diminish, there is a reduction in the permeability of the system to water until, when the inversion point is reached, the system is freely permeable to oil.

Clowes designates substances like NaOH, NaCl, etc., which increase the dispersion of the film in water and increase the permeability of the system to water, as "destructive" agents; $CaCl_2$ and other reagents promoting the water-in-oil type of emulsion he calls "protective," since they diminish the dispersion of the film in water. Osterhout independently reached a similar conclusion to Clowes, finding that electrolytes may be divided into two antagonistic groups, depending on their capacity to increase or decrease the permeability of the protoplasmic membrane in certain biological systems.

Bhatnagar [1] has brought the adsorption film theory to an even more definite form than Clowes. He, too, classified electrolytes into the two main groups mentioned by Clowes, but lays more stress than previous workers on the *wetting* of the adsorbed film.

Pickering first mentioned that the main factor determining the type of emulsion with a given emulsifying agent was the preferential wetting of this agent by oil or water. Bancroft later suggested that the emulsion type was influenced by the relative *solubilities* of the emulsifying agent in oil and water. This, as Bhatnagar points out, "introduces certain complications into our ideas of interfacial tension, and it is by no means easy to understand the two interfacial tensions of a film formed by the concentration of the dissolved substance at the interface according to the Gibbs-Thomson law, and more especially so when the film is assumed to be freely permeable

[1] *J. C. S.*, **120**, 1765 (1921).

to at least one of the two phases of the emulsions." Again, certain multivalent soaps are almost as insoluble in mineral oils and benzene as in water, and certain univalent soaps are both water- *and* oil-soluble. Also, certain substances are soluble either in oil or in water, lowering the surface tension, and yet do not promote emulsions.

Several workers [1] have pointed out that the emulsifying agent must be colloidal in nature. Thus gelatin, casein, albumin, starches, etc., are true colloids. The soaps also furnish colloidal systems, and it is most interesting to note that the sodium salts of the lower fatty acids are not emulsifiers, lauric acid being the first in the series to be effective, and that such salts have been found *not* to yield colloidal solutions, whilst the sodium salts of lauric acid and onwards do.[2] Again, in Pickering's work it was soon evident that the finer the state of subdivision of the solids used, the more perfect was the emulsion ; but the finer the particles become the more nearly do they approach true colloidal suspensions. The colloidal emulsifying agent becomes adsorbed at the dineric interface, forming a film. On the nature of the adsorption of ions by this film will depend the reversal of emulsions by electrolytes. An excess of adsorbed positive ions on this film leads to the formation of water-in-oil emulsion systems ; an excess of adsorbed negative ions produces the opposite type. This rule of Clowes holds good whether the emulsion is stabilised by soluble emulsifying agents like soap or insoluble ones like $Zn(OH)_2$.

On this theory there are no limiting concentrations of oil in water or *vice versâ*, dispersion being independent of the volumes employed. Emphasis is rather laid on the fact that emulsification is influenced by (1) the mass of the emulsifying agent present, (2) the ease with which this agent can be adsorbed at the interfacial separating surface, (3) the nature of the ions adsorbed by the resultant film.

Bhatnagar [3] has made the latest generalisation on emulsion

[1] Cf. Clayton, *J. S. C. I.*, **38**, 113T—118T (1919) ; Briggs, *J. Ind. Eng. Chem.*, **13**, 1008 (1921).
[2] Mayer, Schaeffer and Terroine, *Comptes rend.*, **146**, 484 (1908).
[3] *J. C. S.*, **120**, 1768 (1921).

systems : " All emulsifying agents having an excess of negative ions on them and wetted by water will yield oil-in-water emulsions, while those having an excess of adsorbed positive ions and wetted by oil will give water-in-oil emulsions."

He emphasises that the two main factors governing the process of emulsification are (*a*) the relative wetting power of the two phases with respect to the emulsifying agent, and (*b*) the surface potential of the membrane between the phases. Reversal of phases is considered as being due to changes in this membrane with respect to either or both of these factors.

The purely adsorption view of Bancroft and Clowes may have to be replaced by consideration of electro-capillary adsorption. Due to the adsorption of ions, a contact difference of potential may be set up at the interface, resulting in changes in the interfacial tension apart from those changes due to solute concentration.[1]

Bhatnagar points out that wetting power is connected with interfacial tension,[2] but that our knowledge of the interfacial tension between solids and liquids is very limited ; hence the purely empirical rule formulated above.

The present writer believes that before much further advance can be made towards a general theory of emulsions attention must be paid to the wetting of various emulsifiers by different liquids, and that the important physical factor to be studied is that of the " angle of contact." It is clear, also, that the effect of adsorbed ions on the emulsifying film must be studied, *i.e.*, the angles of contact as influenced by various electrolytes must also be systematically investigated.

Molecular Orientation in the Adsorbed Film.—The interfacial tensions between water and benzene and the influence thereon of sodium and magnesium oleates have been investigated in some detail by Harkins, Davies and Clark.[3] Their results lead them to the conclusion that the *type* of emulsion produced is intimately connected with the *number of oleate*

[1] In this connection cf. Lewis, *Zeits. phys. Chem.*, **83**, 129 (1910).
[2] Cf. Nuttall, *J. S. C. I.*, **39**, 67—71, T. (1920).
[3] *J. Am. Chem. Soc.*, **39**, 586 (1917).

radicles in the molecule of the soap used. On the packing and orientation of the emulsifier (soap) at the dineric interface depends the type of emulsion promoted. The sign and magnitude of the electromagnetic field at the surface of the emulsion globules are also considered to be dependent on the molecular orientation at the interface.

The underlying idea is that for the dispersed globules to be stable the adsorbed molecules (together with adsorbed ions) in the interface must fit the curvature of the drop. For very small drops "the setting and the shape of the molecules becomes of extreme importance in determining both the surface energy and the other electromagnetic energy relations." The conditions for stable emulsions is a zero free-surface energy at the interface drop/continuous phase. This corresponds to the miscibility of two pure liquids whose interfacial tension is very low.

The molecular orientation theory has not only to account for the orientation of solutes at the dineric interface, but has also to deal with the adsorption of finely-divided solids, since numerous instances are known where such solids promote emulsions of the oil-in-water or the water-in-oil type. From Langmuir's work [1] on the adsorption of liquid by a solid it seems likely that the molecules of liquid are orientated, and they pack into the surface layer of a solid, comparable to the packing of oil films on water. Langmuir postulates that "in general there will be a *tendency* for the number of molecules adsorbed to bear a simple integral relation to the number of atoms exposed in the surface of the solid. The configuration of the adsorbed molecules in general are of great influence in determining the number of molecules that can be adsorbed per unit area."

The extension of this theory to solid emulsifiers is that the type of emulsion produced when a finely-divided solid and two immiscible liquids are emulsified together will depend on the molecular orientation of the liquids at the solid/liquid interface. This is, of course, directly connected with the nature of the intermolecular attractions of the solid and liquids. Such

[1] *J. Am. Chem. Soc.*, **39**, 1901 (1917).

attraction we recognise in peptisation and, to a lesser degree perhaps, in wetting. The question of the preferential wetting of the solid now arises, once again leading us to the conclusion that the important factor involved is the angle between the liquid/liquid interface and the solid/liquid interface for the liquid—dispersed or continuous phase—in question.

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CHAPTER VII

PHYSICAL MEASUREMENTS IN EMULSIONS

The study of emulsions in the laboratory frequently involves the determination of interfacial tensions, the nature of the internal or external phase, and the concentration of the emulsion.

The Measurement of Interfacial Tension.—Interfacial tension is the tension existing at liquid/liquid or liquid/solid boundaries, the term surface tension [1] being reserved for the case of liquid/air surfaces. Although the measurement of surface tension is of very great importance in physical chemistry, it does not concern us so much when studying an emulsion. Two liquids, *e.g.*, turpentine and mineral oil, may have the same surface tension,[2] yet against water their interfacial tensions may be very different. Thus the surface tension of turpentine and mineral oil at 20° C. has been given as 31·5 dynes per cm., whilst their respective interfacial tensions against water at 20° C. were 115 and 79 dynes per cm.[3] On the views of molecular orientation as advanced by Langmuir [4] similar liquids, such as vegetable oils, may have the same surface tension against air, owing to the fact that in their surface layers similar groups or portions of the molecules may be similarly orientated. In contact with a given liquid, however, quite different molecular groupings at the separating surfaces may occur, *i.e.*, the interfacial tensions will be different. Since emulsions consist of one liquid dispersed in another liquid, it will be obvious that the liquid/liquid tension is very important indeed.

[1] For discussions on the origin of surface tensions, see the standard works on physics and physical chemistry.

[2] Gardner and Holdt, U.S. Paint Manuf. Assocn., *Circ.* **124** (May, 1921), pp. 1—11.

[3] Gardner and Holdt, *loc. cit.*

[4] *Journ. Amer. Chem. Soc.*, **39**, 1848—1906 (1917).

Practically all the interfacial tension measurements in emulsion studies have been made by a modification of the familiar drop-weight method used in determining the surface tension of liquids against air.[1]

For a drop of liquid hanging from a capillary tube dipping into a second liquid there exists a balance between the weight of the drop and the surface forces supporting it.

If
r = radius of the capillary tube,
d = density of the dropping liquid,
d' = density of the second liquid,
m = weight of the drop,
g = the gravity constant,

then the surface tension T is given by the relation

$$T = \frac{mg}{\pi r}\left(\frac{d-d'}{d}\right).$$

If a volume of liquid, V, falls steadily from the capillary tube into the second liquid, making a total of N drops, it follows that $T \propto \frac{V}{N}$, *i.e.*, the interfacial tension is inversely proportional to the number of drops. For two different liquids, *e.g.*, a vegetable oil and a mineral oil, the relative interfacial tensions against a third liquid, *e.g.*, water will be inversely proportional to the drop numbers obtained.[2]

The method is only used for comparative purposes, and even then is open to objections.[3] For determining absolute tensions several corrections must be made, since the formula has been deduced by applying a statical theory to a dynamic phenomenon.[4] The detachment of a drop of liquid is a complex affair, and widely varying effects may be introduced when pairs of different liquids are under examination. A really satisfying method for measuring the interfacial tension at the liquid/liquid boundary is urgently needed in future quantitative work in colloid studies, especially in emulsions. Several methods

[1] Harkins and Humphery, *J. Amer. Chem. Soc.*, **38**, 236—241 (1916).
[2] Cf. Lewis, *Phil. Mag.*, **15**, 508 (1908); **16**, 467 (1909).
[3] *Vide* Ferguson, *Manchester Memoirs*, **55** (iv.), 14 (1921).
[4] *Vide* Lunn, *J. Amer. Chem. Soc.*, **41**, 620 (1919).

have been suggested by Ferguson,[1] but their application to emulsion systems has not yet been thoroughly investigated.

Since interfacial tension is inversely proportional to the number of drops, it follows that a decrease in this tension will be marked by an increase in the drop number; in other words, a smaller tension supports a smaller weight, hence a given volume of liquid gives more drops. It will now be evident that if a liquid A flows as drops through a liquid B, and the interfacial tension can be reduced, the liquid A will yield a greater number of drops, corresponding to a greater dispersive capacity in liquid B. In other words, the tendency for A to become emulsified in B increases as the interfacial tension decreases. It is in this connection that the drop number furnishes useful data regarding the emulsifying capacities of liquids, though it must again be emphasised that in many cases the results may only be approximate comparisons.

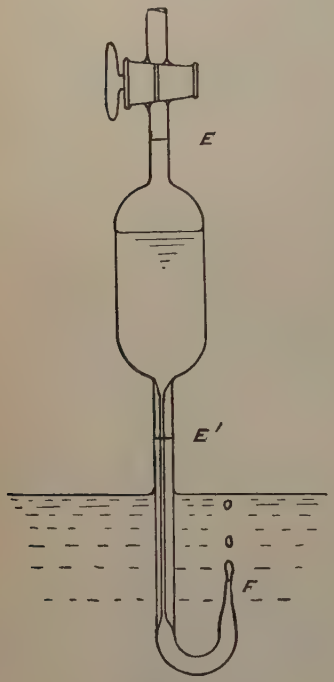

FIG. 12.

Donnan[2] and his pupils determined the drop numbers of various oils against water or aqueous solutions, using a pipette with a curved-up tip, so that the lighter liquid ascended in drops through the denser medium. The drop-pipette (see Fig. 12) consists essentially of a pipette with a bulb whose capacity depends on the liquids under investigation, and may be from 5 c.c. to 40 c.c., between two fixed marks on the stem, E and E'. The length EF is usually about 8 cms. If the relative tensions of, say, oil against soap solutions be required,

[1] *Loc. cit.*, pp. 14 *et seq.*; also *Trans. Farad. Soc.*, **17**, 383 (1922).
[2] *Zeits. phys. Chem.*, **31**, 42 (1899); *Brit. Med. Journ.*, Dec. 23 (1905); *Engineering*, **99**, 551 (1915).

the pipette is filled with oil to the mark E by suction through a side arm, whose tap is then closed. The pipette is carefully wiped at F, and then immersed in the soap solution under test, contained in a glass cylinder which is held in a thermostat at some fixed temperature. The level of the solution above the tip of the pipette is maintained the same in the whole series of determinations made. After the oil and solution have attained the temperature of the thermostat, the main tap is opened and air is very slowly admitted through a fine capillary tube sealed on to the stem of the pipette. Drops of oil should form very slowly—at about twelve seconds' interval—and rise through the solution, their number being carefully counted.

The drop-pipette has been used by numerous investigators on emulsions, particularly by Donnan,[1] Lewis,[2] Shorter and Ellingworth,[3] Clowes,[4] Briggs and Schmidt,[5] Clayton,[6] Holmes and Child,[7] Gardner and Holdt,[8] and Bhatnagar and Garner.[9]

When drops of oil rise through a soap solution there occurs adsorption of soap at the oil/solution interface, and in consequence the interfacial tension is lower than in the case of oil/pure water. If, instead of soap solutions, other colloidal solutions be used, *e.g.*, gelatin, gums, proteins, etc., similar adsorption of the colloid takes place. It is in consequence of this adsorption with the resulting formation of a surface film or envelope,[10] that there arises one of the limiting factors in the general application of the method. Clowes[11] affirms that "the drop method affords an accurate means of determining the exact effect exerted by given substances on the colloidal equilibrium of the interfacial film." This statement, however, needs qualification. In certain cases, the elasticity and strength of the films enveloping the rising drops allows the drops to expand

[1] *Zeits. phys. Chem.*, **31**, 42 (1899).
[2] *Phil. Mag.*, **15**, 499 (1908).
[3] *Proc. Roy. Soc.* (A), **92**, 231 (1916).
[4] *J. Phys. Chem.*, **20**, 426 (1916).
[5] *J. Phys. Chem.*, **19**, 496 (1915).
[6] *Trans. Farad. Soc.*, **16**, Appendix, p. 22 (1921).
[7] *J. Amer. Chem. Soc.*, **42**, 2052 (1920).
[8] Paint Manuf. Assoc. (U.S.A.), Circ. **124** (1921).
[9] *J. S. C. I.*, **39**, 185, T. (1920).
[10] Cf. Harkins, *J. Am. Chem. Soc.*, **39**, 590 (1917).
[11] *Loc. cit.*

and distort and be detachable from the pipette only with difficulty. Thus Briggs and Schmidt observed such disturbances when determining the drop numbers of benzene in aqueous solutions of gelatin and gum arabic. Their experience led them to the conclusion that "drop numbers are not a fair and sufficient test for an emulsifier in solution." In such cases drop-number determinations fail to give an accurate measure of the ability of the solution to emulsify oil or other disperse phase.

The drop method gives useful comparative data when the results obtained can be repeated and confirmed. Thus Clayton[1] was able to repeat his results within half a drop. His work, however, was mainly concerned with the drop numbers of pure edible oils and fats in distilled water, where disturbing film formation would be at a minimum. On the other hand, Briggs and Schmidt, in determining the drop number of benzene in 1 per cent. gelatin solution, obtained values ranging from 23 to 32, an obviously unsatisfactory result.

The drop method is interesting owing to the part it has played in the development of our present knowledge of emulsification and emulsions, but it will undoubtedly be replaced in future work by a method of greater accuracy and one uninfluenced by the character of the interfacial adsorbed film.

The Determination of Phases.—It is frequently necessary in work on emulsions to determine which of the two liquid phases is the continuous and which is the dispersed phase. Since with oil and water two types of emulsion are possible, oil-in-water and water-in-oil, a ready and accurate means of differentiating between these types is very desirable. Particularly is this the case when studying the problem of the reversal of phases. Three methods have been proposed :—

(a) **The Indicator Method.**—Robertson[2] suggested the use of an oil-soluble, water-insoluble dye, Sudan III. This red dye, as a finely-divided solid, is dusted on to the surface of the emulsion to be examined. If the oil phase be continuous, then the dye will gradually spread throughout the system owing to

[1] *Loc. cit.*
[2] *Koll. Zeits.*, **7**, 7—10 (1910).

its dissolving in the oil. If, however, water or aqueous solution be the continuous phase, then the dye will not spread, being confined to those globules of oil with which it comes into immediate contact. This method is useful in dealing with solid emulsions like butter and margarine, which are to be examined under the microscope. Thus Palmer [1] used acetone solutions of Sudan III. and fuschin to stain the butterfat globules in cream, and was able to prove the inversion of phases on churning. For emulsions in general there are objections to the use of added organic substances which may exert a new influence on the system.[2]

Newman [3] used this method with emulsions of benzene and water, employing iodine and methyl orange, the former soluble in benzene, the latter soluble in the water phase. Hall [4] employed the indicator method for emulsions of water in various organic liquids, using the water-soluble dye Nilblau and the oil-soluble dyes Scharlach Roth (Grubler) and dimethyl-amido-azo-benzene (Merck).

(b) **The Drop-dilution Method.**—The principle of this method is that an emulsion can be diluted by addition of the external or continuous phase, but not by adding the dispersed phase. Pickering [5] first recognised the principle, pointing out that an emulsion containing 99 per cent. by volume of mineral oil in 1 per cent. soap solution "will mix perfectly with water to form a weaker emulsion, but will not mix with more paraffin."

Briggs [6] suggested that the phase relationships of an emulsion could be determined by placing a drop of emulsion in a little water, and stirring. If the emulsified particles spread in the water, then water is the external phase ; if no spreading occurs, then water is the internal phase.[7]

Newman [8] found this method much more reliable than the

[1] Missouri Agr. Expt. Sta., *Bull.* **163**, 40 (1919).
[2] Cf. Clowes, *J. Phys. Chem.*, **20**, 445 (1916).
[3] *J. Phys. Chem.*, **18**, 34 (1914).
[4] *J. Phys. Chem.*, **21**, 616 (1917).
[5] *J. C. S.*, **91**, 2002 (1907).
[6] *J. Phys. Chem.*, **18**, 34 (1914).
[7] *Vide* also Holmes and Cameron, *J. Amer. Chem. Soc.*, **44**, 67 (1922).
[8] *J. Phys. Chem.*, **18**, 34 (1914).

indicator method. Hall [1] proposed a modification of the test for not too opaque emulsions. A drop of one of the liquids is placed in the emulsion near to the glass wall of the container. If the liquid is the dispersed phase "it is clearly delimited and moves up or down through the emulsion." If it be the continuous phase, it rapidly diffuses into its surroundings, making a slightly less opaque area. In the case of emulsions of water in hydrocarbon oils, as obtained by Hall, water sinks as a clear drop, whereas oil rises and diffuses.

(c) **The Electrical Conductance Method.**—This method, proposed by the writer,[2] is based upon the fact that an oil-in-water type of emulsion, particularly when the aqueous phase contains small quantities of electrolytes, will show an electrical conductivity, whilst water-in-oil emulsions, characterised by having oil—an electrical insulator—as the continuous phase, will not conduct electricity. Sherrick [3] used this method in his investigations of crude mineral oil emulsions containing water as the internal phase. Bhatnagar [4] has demonstrated the great utility of the electrical method, and found it to be very sensitive indeed. He examined his emulsions in a bottle fitted with two platinum electrodes fixed at a constant distance apart. The application of a constant voltage for a second or two produced a current (measured in milliamps) with all emulsions of the oil-in-water type. Emulsions of the opposite type allowed only—if at all—a very small current of the order of 0·1 milliamp, as against currents of 10 to 13 milliamps for the oil-in-water emulsions. The reversal point could thus be readily detected, and in all Bhatnagar's studies on emulsion reversals this method was used.

Nephelometry.—The oil content of an emulsion may be estimated by "breaking" the emulsion, *e.g.*, by adding a solution of alum and then extracting with ether. In certain cases, however, the concentrations of given emulsions may be compared by measuring the turbidity of the samples under standard conditions. Various instruments have been proposed

[1] *J. Phys. Chem.*, **21**, 617 (1917).
[2] *Brit. Assoc. Colloid Reports*, **2**, 114 (1918).
[3] *J. Ind. Eng. Chem.*, **12**, 135 (1920).
[4] *J. C. S.*, **117**, 542 (1920).

for work in this connection, known as nephelometers, turbidimeters, and tyndallmeters. The method is based on the measurement of the brightness of a given depth of emulsion viewed at right angles to the beam of light illuminating the emulsion.[1] The intensity of the light reflected from the particles suspended in an emulsion varies with the number and average diameter of the globules.

The general principle will be understood from the diagrammatic sketch in Fig. 13. If A and B are two tubes containing

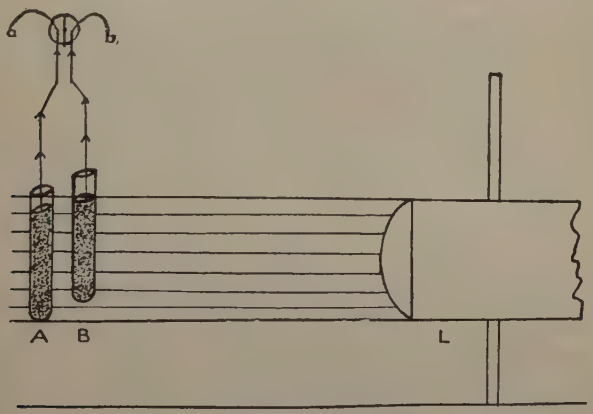

FIG. 13.

emulsion or suspension and L is a beam of light projected on to the tubes at right angles, then *a* and *b* will be the light in the eyepiece due to reflections from the suspended particles. If the tube A contained distilled water, then, provided the instrument be perfect, no light at all should be visible at *a*. The light at *a* due to reflection is always compared with *b*, and never measured absolutely. Tube B should contain a standard emulsion, *i.e.*, the oil concentration is known.

Nephelometers are now in use which permit accuracy in measurements of the concentration of suspensions and emulsions. Simply, the instrument has two tubes surrounded at the bottom by two tubular metal light shields. The two

[1] An excellent account of the nephelometer is given by Kober, *J. Ind. Eng. Chem.*, **10**, 556 (1918).

liquids, one standard, the other under investigation, are placed in the respective tubes and illuminated by a suitable light source (*e.g.*, a 250-watt Mazda lamp) mounted in the focus of a pair of condensers, so that a beam of parallel rays is projected horizontally into the tubes. All extraneous light is cut off by boxing and screening. By means of racks and pinions, the tubular light shields are adjusted in a vertical direction until the two tubes are equally illuminated as seen in the two fields in the eyepiece.

In the Kober-Klett type of nephelometer,[1] instead of movable tubes of metal serving to cut out light (*i.e.*, to expose a smaller depth of liquid to the light rays), metal plungers are used which can be moved up or down in the liquids contained in cups. The downward motion of the plunger causes liquid to rise inside the metal plunger, so that the depth of liquid exposed to the light rays is lessened. A later type of instrument [2] provides for stationary plungers and movable cups.

In using a nephelometer a calibration curve is frequently used instead of resorting to mathematical formulæ. For example, to obtain this curve for the latter type of nephelometer, the cups are filled with the standard emulsion and placed in position in the instrument. The left-hand cup is adjusted until the scale reading is exactly 20·0, and the position of the right-hand cup is then adjusted until both sides are equally illuminated, the average of several readings being taken. This setting of the right-hand cup is retained for the whole series of comparisons with the standard.

The left-hand cup is now nearly filled with a diluted solution of the standard. After placing in position, the height is adjusted until illumination on both sides again becomes equal, and the scale reading is read. In this way the standard emulsion is compared with 0·9 standard, 0·8 standard, 0·7 standard, 0·6 standard, and 0·5 standard, and the results plotted. The ordinates express nephelometric scale readings, and the abscissæ express the ratio of the emulsion concentrations. With the aid of such a graph the concentration of an

[1] *J. Ind. Eng. Chem.*, **10**, 556 (1918); cf. also Kober and Graves, *ibid.*, **7**, 843 (1915).

[2] Kober, *Journ. Biol. Chem.*, **29**, 155 (1917).

unknown emulsion may be readily ascertained, since the scale reading (ordinate) will have been determined.

Bloor [1] has used the nephelometer for the determination of fat in milk, using emulsions of triolein in water as standards. He could easily determine 0·05 mg. of fat, and even 1 part in a million produced a marked cloud. Woodman, Gookin, and Heath [2] used a similar method for the essential oils.

Ellis [3] determined the mean radius of the globules of various emulsions by means of the nephelometer. For this purpose he estimated the relative turbidities of different samples of emulsions of acid-free cylinder oil in water, of concentration about 1 in 10,000. The concentration was kept constant, but the mean size of the oil globules was varied. The results were expressed graphically, the abscissæ being globule radii, and the ordinates the relative turbidities. The turbidity of an emulsion with an average globule radius of 1×10^{-4} cm. served as the standard unit.

The theory underlying nephelometry, viz., the optics of turbid media, is very complicated and still somewhat vague. An attempt to replace the purely empirical connection between the concentration, grain-size, and other properties of emulsions and suspensions has recently been made by Wells,[4] who shows that many secondary effects complicate the phenomena of diffuse reflection and transmission. His paper should be consulted for the mathematical treatment involved.

[1] *J. Amer. Chem. Soc.*, **36**, 1300 (1914).
[2] *J. Ind. Eng. Chem.*, **8**, 128 (1916).
[3] *Zeits. phys. Chem.*, **80**, 597 (1912).
[4] *J. Amer. Chem. Soc.*, **44**, 267—276 (1922); cf. Mecklenburg, *Koll. Zeits.*, **15**, 149 (1914); **16**, 97 (1915).

CHAPTER VIII

EMULSIFICATION

EMULSIFICATION is the art or practice of dispersing a given liquid as more or less permanent globules in another liquid medium. Stable emulsions of low oil concentration may be obtained by boiling a little oil in water for some time,[1] by dissolving oil in an organic liquid and then "precipitating" this solution in water,[2] or by steam distillation (*e.g.*, of aniline). To make concentrated emulsions a suitable third substance must be added.

Emulsification is very important industrially, and numerous machines have been devised with a view to securing an intimate subdivision of the disperse phase in the continuous medium. The general principle involved is agitation of the two liquids either by means of revolving baffle plates or specially-designed stirrers, *e.g.*, screw propellers, worm screws, injectors, etc. The containing vessels are usually double jacketed, so as to permit of temperature regulation by circulating steam or hot or cold water, as required. Usually emulsions are made in batches in tanks, but continuous-flow emulsifiers[3] are now being introduced in many works.

What we may term the mechanics of emulsification is far from being understood even now, although numerous emulsions of widely varying nature are made in everyday industrial operations. Some very strange phenomena have been reported concerning the making and "breaking" of emulsions by simple mechanical methods. Thus, Ayres[4] mentions the case of an oil-field emulsion, so stable as to defy separation in a centrifuge, being quite separated into water and oil after transit in

[1] Lewis, *Koll. Zeits.*, **4**, 211 (1909).
[2] Lewis, *loc. cit.*
[3] *Vide* Clayton, "Margarine" Longmans), 1920, p. 71.
[4] *J. S. C. I.*, **35**, 678 (1916).

an express train. In some peculiar way the vibration of the train had caused the emulsion to break. Again, Nugent [1] observes that an emulsion of 50 per cent. benzene in water containing 0·4 per cent. gelatin, which was stable to centrifuging at 2,000 revolutions per minute, could be separated by attaching a tube containing the emulsion to the spoke of a wheel which rotated in a vertical plane at a rate of three revolutions per minute. In this case no separation occurred unless there was an air space in the tube, when the rate of separation depended directly upon the size of this air space. What is probably involved here is the Ramsden phenomenon of the concentrating of the emulsifying agent at the interface, air/continuous phase. The principle has been used by Clavel,[2] Karpinsky,[3] and Edser [4] for separating emulsions. Edser finds that the extent of the separation of oil from wool-washing effluent depends on the extent of the air/liquid interface, and that a certain minimum time of contact between the air and emulsion is necessary.

The prevalent idea regarding emulsification is that the oil and aqueous phases should be agitated together as violently as possible, so that small globules might result, thus tending towards a more stable emulsion. Consequently an empirical limit only is set on emulsification practice,[5] which is greatly in need of thorough investigation on the effects of different methods of agitation, and the degree of any one kind, on mixtures of oils and aqueous phases. It is well known that one can both make and " break " an emulsion by agitation. Thus Sheppard,[6] working on the emulsification of nitrobenzene in sulphuric acid, found that " de-emulsification was accelerated by slow shaking, or even single vibration in some cases, for emulsions which remained stable at rest, while shaking gently at slightly higher frequency would re-emulsify, to a system again stable at rest." Ayres [7] found that agitation (within reasonable

[1] *Trans. Farad. Soc.*, **17**, 703 (1922).
[2] Brit. Pat. 177498 (1922).
[3] Ger. Pat. 314090 (1918).
[4] Brit. Pat. 157490 (1922).
[5] *Vide* Clayton, " Theory of Emulsions and Margarine Churning," *Margarine Journal*, **2** (13), 503—4 (1920).
[6] *J. Phys. Chem.*, **23**, 634 (1919).
[7] *Chem. Met. Eng.*, **22**, 1059 (1920).

limits) tends rather to increase than to diminish the size of globules of oils emulsified in aqueous soap solutions. This effect is somewhat comparable to the formation of butter from

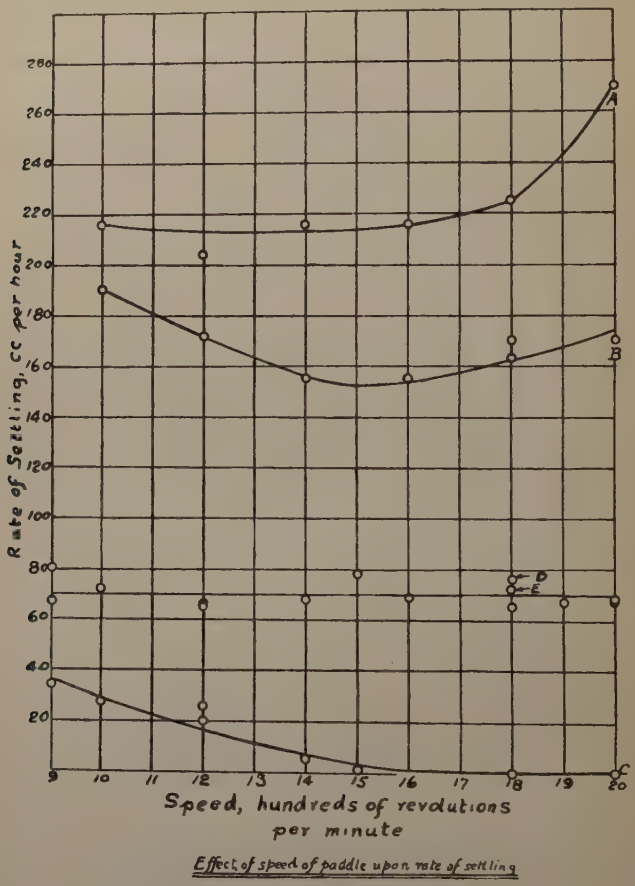

FIG. 14.

cream by churning, *i.e.*, by prolonged agitation. As Scoville[1] has pointed out, "oil may be separated from a good emulsion by over-manipulation."

Another instance of a limiting degree of agitation in emulsification is given by Nugent,[2] who found that gentle

[1] Scoville, "The Art of Compounding" (1895), p. 82.
[2] *Loc. cit.*

agitation favoured the formation of emulsions of benzene in aqueous gelatin ; vigorous shaking (under the conditions of his tests) caused de-emulsification.

It is quite reasonable to believe that for any given emulsifying apparatus there exists an optimum speed or degree of agitation or mixing, and an optimum time of running, whereby the most perfect emulsion can be attained for a given system.[1] Experiments prove this to be correct. Bechold, Dede and Reiner[2] found that the formation of emulsions of water and organic liquids plus finely-divided solids reach an optimum after ten minutes' standard shaking.

Herschel,[3] in his studies on the resistance of lubricating oils to emulsification in water, has investigated the effect of duration of stirring and of speed of agitation. He adopted five minutes as the time for agitation (using an electrically-driven paddle) in all his tests, having found that no marked increase in stability of the resultant emulsions followed longer agitation. In regard to the speed of stirring his mixtures of five different oils and water, he found that, in general, there is a speed above which the stability of the emulsions decreased, *i.e.*, the curve representing the relation between speed and stability passes through a minimum. Fig. 14 is reproduced from Herschell's paper ; the abscissæ represent speed in hundreds of revolutions per minute, whilst the ordinates measure stability in terms of the number of cubic centimetres of clear oil rising to the top of the emulsion per hour. He adopted a speed of 1,500 r.p.m. as giving, on the average, a minimum rate of settling.

Briggs and Schmidt[4] have studied various factors influencing the emulsification of benzene in 1 per cent. sodium/oleate solution, and found that the results depended on the size and shape of the containers and the speed and mode of agitation. Some interesting determinations were made of the time required to emulsify completely mixtures, containing different relative

[1] *Vide* Newman, *J. Phys. Chem.*, **18**, 38 (1914) ; also Pollard, *Pharm. J.*, **83**, 135—39 (1909).
[2] *Koll. Zeits.*, **28**, 7 (1921).
[3] U.S. Bureau of Standards, Technological Papers No. **86**, pp. 1—37 (1917).
[4] *J. Phys. Chem.*, **19**, 478 (1915).

amounts of benzene and soap solution, at room temperature, keeping the combined volumes of benzene and soap solution constant at 50 c.c. The emulsions (oil-in-water type) were made in 125 c.c. bottles placed in a shaking machine, giving a lateral motion of approximately 400 oscillations per minute. It was found that the amount of shaking required increases, at first slowly with increasing volumes of benzene, and then rapidly, until the amount of shaking required becomes infinitely great.[1] Fig. 15 is the graph obtained by plotting the following results, the ordinates representing per cent. by volume of benzene, and the abscissæ the time in minutes required for complete emulsification.

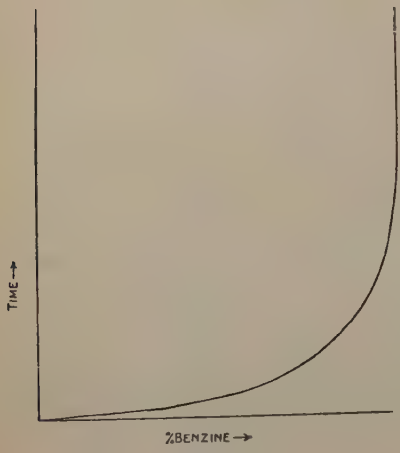

FIG. 15.

Per cent. Benzene (by Volume).	Time (in minutes) for Complete Emulsification.
99 ..	Incomplete after eight hours.
96 ..	125
95 ..	40
90 ..	23 (22)
80 ..	17 (11)
70 ..	10
60 ..	7
50 ..	3
40 ..	2
30 ..	<1

From the graph the practical significance of such results is obvious, inasmuch as the excessive expenditure of power in making an emulsion is unnecessary, an optimum working time being readily ascertained.

[1] Cf. *J. Phys. Chem.*, **24**, 120 (1920).

These results would, of course, be altogether different if the increasing volumes of benzene had been added *gradually* instead of in bulk. Indeed, the only reliable method of obtaining stable concentrated emulsions is to add the disperse phase gradually, agitating at the same time.[1]

Moore [2] has investigated the effect of the time of mixing on the size of aqueous globules dispersed in kerosene, using lamp-black as the emulsifying agent. He found that the size of the water droplets for any given mixture of ammonium chloride solution, kerosene and lamp-black, passes through a minimum when the time of stirring is varied. The following table exemplifies the results obtained :—

10 c.c. kerosene.
30 c.c. N/1.NH_4Cl.

Weight of lamp-black.	Time Mixed. Minutes.											
	15.		30.		45.		60.		75.		90.	
grs.	Diameter in mm.	Average deviation per cent.	Diameter in mm.	Average deviation per cent.	Diameter in mm.	Average deviation per cent.	Diameter in mm.	Average deviation per cent.	Diameter in mm.	Average deviation per cent.	Diameter in mm.	Average deviation per cent.
0·4	·0551	35·2	·0590	33·0	·0484	24·8	·0504	38·7	·0637	58·8	·0949	41·0
0·6	·0452	20·3	·0400	31·2	·0432	46·3	—	—	·0490	17·0	·0697	42·8
0·8	·0367	30·6	·0338	25·7	·0250	20·9	·0337	41·2	·0265	49·6	·0309	46·3

Interesting work on emulsification has been carried out by Briggs,[3] who, arguing that the *mode* of shaking a mixture of benzene and sodium oleate might be an important factor in emulsification, found that *intermittent* shaking was vastly more effective than the usual uninterrupted agitation. Briggs concluded that "intermittent shaking may be six hundred or even a thousand times more effective than uninterrupted but equally violent agitation."

Shaking by hand, mixtures of benzene in 1 per cent. aqueous sodium oleate, Briggs found that to emulsify 60 per cent. by

[1] Cf. Blichfeldt, Brit. Pat. 8227 (1912).
[2] *J. Am. Chem. Soc.*, **41**, 944 (1919).
[3] *J. Phys. Chem.*, **24**, 120 (1920).

volume of benzene 750 shakes were necessary, occupying 4·2 minutes without stopping. The same mixture could be completely emulsified with 5 shakes in less than 1 minute, if after 2 shakes a rest of 30 seconds was allowed. Similarly, to emulsify 80 per cent. by volume of benzene 6,300 shakes, occupying 35 minutes, were required when shaking continuously, but only 45 shakes over a total period of 4½ minutes were necessary when 30 seconds' rest followed each 2 shakes.

The effect of varying the rest interval was also studied, emulsions being made of 90 volumes of benzene in 10 volumes of 1 per cent. sodium oleate, shaking once up and down by hand.

Rest Interval. Secs.	Total Shakes Required.	Total Time Elapsed. Minutes.
60	12	12
30	18	10
10	31	6
Nil.[1]	9,900	>60

From these results it is seen that the time required to form a complete emulsion with intermittent agitation passes through a minimum as the rest interval increases.

The explanation advanced by Briggs, to account for the very marked superiority of intermittent over continuous emulsification, is that efforts should be made to break up only the disperse phase of an emulsion, leaving the continuous phase as unbroken as possible ; anything tending to disintegrate the continuous medium—sodium oleate solution in these experiments—will retard emulsification. Since globules of benzene in a soap medium are prevented from coalescing, it is obviously advantageous to keep the soap medium as continuous as possible. In uninterrupted shaking some time must elapse before the soap solution is really disintegrated into drops, and hence the dispersion of benzene in the solution should be more rapid and effective during the initial stages of emulsification. This is found to be the case in actual practice.

The present writer believes that Briggs' explanation is only

[1] Uninterrupted shaking for over one hour.

partially true. Shaking is an inferior method of making emulsions, because, as the emulsion becomes more perfect, the smashing action between the relatively heavy and light particles becomes more feeble, whereas the smashing forces should be increased. Accordingly, continuous shaking should give equally as good results as the intermittent shaking, provided the emulsified portions of the mixture are continuously removed from the mass, so that the energy of shaking is concentrated on the remainder. A centrifugal type of emulsifier might be developed to realise such emulsification.

Pharmaceutical emulsions are made by triturating in a mortar according to one of two methods—the English and the Continental. In the former the emulsifier, *e.g.*, gum acacia, is ground to a mucilage with water, and then the oil and the remainder of the water are added, in small portions alternately, triturating after each addition. The method is unsatisfactory,[1] and inferior to the Continental method previously described.[2]

Homogenisation.—Emulsions, whether prepared in the laboratory or in technical practice, usually contain dispersed globules of very different diameters. The process of subsequently reducing these globules to an approximately equal diameter many times smaller than the average previously attained in the emulsion is termed homogenisation, and the resulting product is called a homogenised emulsion.

Homogenised emulsions are obviously advantageous in scientific investigations, and will undoubtedly be employed in future researches much more frequently than hitherto. At the moment, however, their utility is more recognised industrially, particularly in dairy work, where homogenised cream and milk have long been familiar products.

Hatschek [3] has shown that subdivision of emulsified globules demands a force which increases enormously as the size of the globules decreases. Laboratory homogenising apparatus is rather unusual as yet and somewhat unsatisfactory, considering what can be accomplished with modern machines in dairies.

[1] Arny, "Principles of Pharmacy" (1911), p. 267.
[2] See p. 44.
[3] *Koll. Zeits.*, 7, 81 (1910).

Briggs [1] devised a simple type of homogeniser by means of which he was able to reduce the particles in hand-shaken emulsions from an average diameter of 25 μ to 5 μ. Repeated homogenisation decreased the average diameter to between 2 and 3 μ. These emulsions then showed greatly increased stability.

Fischer and Hooker [2] obtained good results in the laboratory by passing coarse-grained emulsions through a pestle and mortar arrangement. The emulsion is poured into a metal funnel, within which is turned a pestle. Upon this pestle any amount of pressure may be exerted by means of a screw at the top. The emulsion passes under hydraulic pressure between the grinding surfaces, which, being bevelled, causes the emulsion globules to be decreased in size before passing through the exit.

In 1892, Paul Marix [3] obtained two French patents in connection with the manufacture of margarine for making emulsions by passing the ingredients under pressure through a fine orifice. Later [4] he proposed that the liquids to be emulsified should be finely divided and intimately mixed by rubbing against a moving surface ; under centrifugal force the liquids passed between a stationary plate and a rapidly-revolving plate. Julien [5] adopted the principle of Marix's patent, but forced the liquids through a *series* of small holes. The subdivision of the globules in an already existing emulsion, *e.g.*, milk, with a view to stabilising it was then conceived by Gaulin.[6] He employed a bundle of capillary tubes, against one end of which a powerful spring pressed a concave valve ball. A pressure of 250 atmospheres was required to force the milk (at 85° C.) through these tubes, whereby homogenisation was successfully achieved.[7] Later, agate was substituted for metal, owing to the excessive wear of the latter.[8]

Schröder and Wrede proposed a similar machine, but substi-

[1] *J. Phys. Chem.*, **19**, 223 (1915).
[2] " Fats and Fatty Degeneration " (New York, 1917), p. 24.
[3] Fr. Pats. 218946-7 (1892).
[4] Fr. Pat. 221583 (1892).
[5] Fr. Pats. 220446 (1892), 224553 (1892).
[6] Fr. Pat. 295596 (1899).
[7] Cf. also Bonnet, Fr. Pat. 333501 (1903), and Répin, Fr. Pat. 328064 (1902).
[8] Cf. Talansier, Brit. Pat. 19626 (1909).

tuted for the tubes an agate shaft with spiral grooves cut in the surface, which caused the shaft to revolve as the milk was forced through under a pressure of 150 atmospheres. Schröder [1] later replaced the revolving valve with an adjustable stepped valve, in which the face of each succeeding step was closer to the seat, thus providing for a gradual breakdown of the globules.

The Gaulin machine [2] is in extensive use and is very efficient. A description of this machine will suffice as being typical of homogenisers in general.[3]

The plant comprises a triplex pump, each cylinder possessing

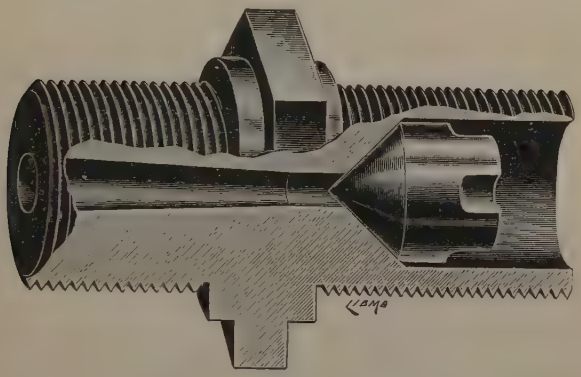

FIG. 16.—Homogenising Valve.

a suction and discharge valve, capable of withstanding very great pressures. In the discharge pipe is placed the agate homogenising valve, carefully ground into the seat and held close by a spring. The valve (comparable to a relief valve) is set to open at 2,000~3,000 lbs. per square inch. When during working the pressure reaches a point where the homogenising valve is forced open, the space between the disc and the seat is so narrow that the fat globules in an emulsion (milk or cream) are subdivided to such a degree that a new emulsion of remarkable stability results. Any desired pressure, according to the degree of subdivision required, can be immediately

[1] Ger. Pat. 277225 (1912).

[2] *Vide* Fr. Pat. 323875; Brit. Pat. 22875 (1904); U.S. Pats. 753792 (1904), 756953 (1903).

[3] Cf. *Chemische Apparatur*, **3**, 133 (1916), and *Pharm. Journ.*, **36**, 734 (1913), for descriptions of homogenising machines.

obtained by regulating a hand-wheel attached for this purpose to the homogenising head. Fig. 16 shows the arrangement

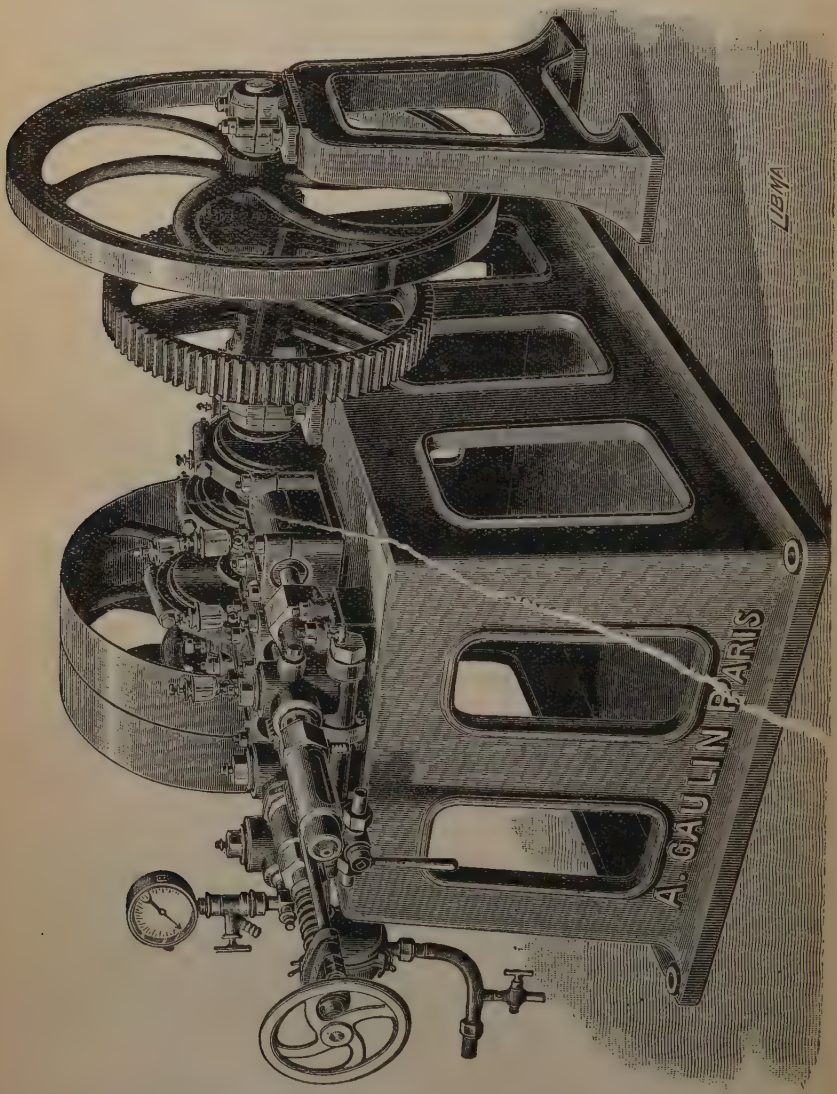

Fig. 17.—Homogenising Machine.

of the agate valve in the discharge pipe, and Fig. 17 illustrates a machine capable of homogenising 550 gallons of milk per hour, requiring 18—20 h.p.

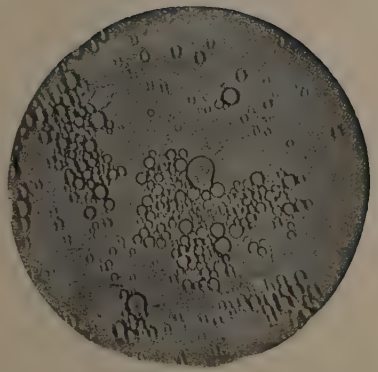

Fig. 18A.—Milk in its Natural State.

Fig. 18B.—Milk Homogenised, showing the Increased Dispersion of the Fat Globules.

To face p. 121.

During the homogenisation of milk or cream the liquid is pre-heated to 60° C., and a pressure of about 3,000 lbs. per square inch is maintained. The diameters of the raw milk-fat globules vary between 0·01 mm. and 0·0016 mm., the size depending on such factors as the breed of cattle, feeding, time of the year, etc. In cream the fat globules have diameters ranging from 0·003 mm. to 0·005 mm. The process of homogenisation reduces the diameters of the fat globules in milk or cream to about one-hundredth of their original value (see Fig. 18). Such homogenised emulsions are wonderfully stable, and usually defy separation even when centrifuged.

The stability of homogenised milk with respect to the separation of the butter-fat has been studied by Sobbe.[1] Two samples of milk were homogenised, and allowed to stand in a measuring cylinder at room temperature for seventy-two hours, a little formaldehyde being added as preservative. Analyses of the fat contents at various levels were then made, and the following results obtained :—

Sample.	Milk A.		Milk B.	
Initial Fat Content.	2·6 per cent.		3·3 per cent.	
Per cent.	Raw.	Homo-genised.	Raw.	Homo-genised.
Fat in lower, 50 c.c.	0·3	2·3	0·2	2·95
Fat in middle, 50 c.c.	1·4	2·5	0·6	3·20
Fat in upper, 50 c.c.	8·5	2·9	14·5	3·85

Very little creaming takes place in the case of homogenised milk, whilst raw milk creams rapidly. Homogenised milk cannot be churned into butter, and homogenised cream cannot be whipped ; the addition of a colloid such as gum tragacanth is necessary, if a permanent foam is desired. The Brownian movement is very marked, and there is a measurable decrease in the surface tension.

The cause of these remarkable changes is the increased

[1] *Milchwirtsch, Zentr.*, **43**, 503—6 (1914).

adsorption of casein on the fat globules. Since the number of fat globules has increased about a thousand times, the adsorbing surface created is enormous. The adsorption of casein is at once manifested by the large increase in viscosity, homogenised milk and cream being much thicker than the original liquids. Wiegner [1] reduced the average diameter of the fat particles in milk from 2·9 μ to about 0·27 μ, and from viscosity measurements calculated that, of the casein in milk, 2·27 per cent. was adsorbed in the ordinary sample and 25·2 per cent. in the homogenised milk. (This is based on the assumption that only casein is adsorbed and that the mean thickness of the adsorbed layer is 6·8 $\mu\mu$.) Skim milk cannot be homogenised, since it is practically fat free and the casein is already present in a high degree of dispersion.

That adsorption is the main factor in homogenised emulsions has also been shown by Briggs,[2] who investigated emulsions of benzene in dilute solutions of sodium oleate. The quantity of soap removed from solution, being a function of the interfacial area of separation between water and benzene, was greatly increased as the emulsions were progressively homogenised. Unfortunately, the quantitative determination of the relation existing between the specific surface and the amount adsorbed was not carried out.

Wiegner,[3] in his studies on homogenised milk, investigated the change in the diameters of the fat globules and the increase in their numbers following homogenisation. The following table shows the results obtained :—

Samples.	Specific Gravity.	Per cent. Fat.	Diameter of Fat Globules.		Number of Fat Globules per 100 c.c.	
			Normal.	Homogenised.	Normal.	Homogenised.
1	1·0313	3·17	2·86 μ	0·27 μ	$2{\cdot}87 \times 10^{11}$	$3{\cdot}41 \times 10^{14}$
2	1·0320	2·87	2·94 μ	0·17 μ	$2{\cdot}40 \times 10^{11}$	$3{\cdot}02 \times 10^{14}$

The number of particles in the first sample has increased

[1] *Koll. Zeits.*, **15**, 105 (1914).
[2] *J. Phys. Chem.*, **19**, 229 (1915); cf. Martici, *Arch. d. Fisiol.*, **4**, 133 (1907).
[3] *Koll. Zeits.*, **15**, 105 (1914).

1,188 times, and in the second sample 1,258 times, after homogenisation. The surface area of the fat globules has been increased 112 and 117 times respectively. The viscosities of the samples of raw and homogenised milks were in the ratio of 1 : 1·12 and 1 : 1·15 respectively. There was no apparent change in density and no difference in electrical conductivity, though Buglia,[1] in similar work, noted a slight increase in the electrical conductivity of homogenised milk. Both Wiegner and Buglia find that there is a slight decrease in osmotic pressure following upon homogenisation.

Homogenised milk and cream are more easily digested than the usual products, owing to the fine subdivision of the fat globules,[2] and are thus valuable in infant feeding. They look and taste richer than the ordinary commodities, *e.g.*, new milk of 4 per cent. fat content has, after homogenisation, the appearance of a cream containing 8 per cent. fat, and a 15 per cent. cream, after homogenisation, is a good substitute for a 25 per cent. cream in culinary operations.

In America homogenised cream is extensively used in the manufacture of ice-cream, where a smooth texture is demanded.[3] Ordinarily, ice-cream, unless containing a protective colloid like gelatin or egg-albumin, becomes grainy, due to the formation of ice crystals, and so tastes gritty. With homogenised cream a better ice-cream can be made, since the spaces between the now very numerous fat globules are so small that the ice crystals are too small to be noticeable.

[1] *Koll. Zeits.*, **12**, 353 (1908).
[2] Cf. Bechold, "Colloids in Biology and Medicine" (N.Y., 1919), p. 175.
[3] Cf. Clayton, *Brit. Assoc. Colloid Report*, **2**, p. 116 (1921).

CHAPTER IX

DE-EMULSIFICATION

WHILST the problem of making stable emulsions figures prominently in many industrial operations, the converse problem of "breaking" emulsions is also important. Only too frequently emulsions are found as undesirable factors in certain technical process, and methods for their de-emulsification or separation demand much thought and ingenuity. Just as no absolutely general rule can be formulated for making any kind of emulsion at all, so no general rule obtains for breaking any given emulsion. Each system presents its own inherent difficulties, so that where a certain scheme operates successfully with some emulsions the same scheme may be quite ineffective for other emulsions. A universal method of de-emulsification has yet to be found.

Well-known instances where de-emulsification is practised are the separation of water from crude petroleum emulsions, the separation of oil from condenser water, and the making of butter, this latter involving the preliminary separation of cream from milk.

Oil-field Emulsions.—During the drilling operations into the oil sands when boring for petroleum there occurs infiltration of water, which becomes emulsified in the oil, producing water-in-oil emulsions of varying degrees of stability. The larger globules of water eventually settle out as "free water," but the more minute globules remain in suspension, and are termed "trapped water." The water content ranges from traces to 60 per cent., the usual figure being 25 per cent. Crude oil, to be saleable or classed as "pipe line" oil, must not contain more than 2 per cent. of water, an arbitrary limit fixed by the transporting companies.

It has been proved by Sherrick,[1] in the case of Goose Creek

[1] *J. Ind. Chem.*, **12**, 133—139 (1920).

(Texas) field oils, that the oil is the continuous phase, the water being dispersed in this as globules bearing a negative charge. Sherrick used the electrical conductivity method to determine the type of emulsion,[1] the method being particularly suitable in this case for determining the phase relations of the oil and water, since the latter contains dissolved electrolytes (particularly NaCl), sometimes up to 10 per cent. concentration. If the aqueous solution were the external phase, the emulsion should readily conduct electric current. In Sherrick's tests, however, with electrodes 2 inches apart and a P.D. of 250 volts applied, no deflection was observed of the needle of a sensitive milliammeter placed in the circuit. A cataphoresis test confirmed the conclusion that water was the dispersed phase.

The emulsifying agent serving to stabilise crude petroleum emulsions is probably asphalt, either alone or adsorbed on clay and other earthy matter. We have already seen that clay does promote the emulsification of water in oil.[2] Asphalt in its relation to the colloid chemistry of petroleum has been discussed by Dunstan,[3] Richardson,[4] Sherrick,[5] and Padgett.[6] It seems fairly agreed by these authorities that asphalt or other heavy hydrocarbons present in crude oils may be adsorbed on the earthy matter present, and this complex then forms a protective film about the water globules.[7] That asphalt can act as an oil-soluble colloid promoting emulsification has been shown by Sherrick,[8] who prepared an emulsion of NaCl solution in pure white paraffin oil by using 0·5 per cent. asphalt. Again, Richardson [9] has found that the earthy matter in Trinidad asphalt possesses a high adsorption capacity for the bitumen in the asphalt.

Oil-field emulsions are separated, and the dry oil recovered by many process, which, however, fall into three main classes :

[1] See p. 106.
[2] See p. 7.
[3] *Brit. Assoc. Colloid Repts.*, **3**, 91—98 (1920).
[4] *Brit. Assoc. Colloid Repts.*, **3**, 98—102 (1920); *Met. Chem. Eng.*, **21** (Jan., 1917).
[5] *Loc. cit.*
[6] *Chem. Met. Eng.*, **25**, 189—192 (1921).
[7] *Vide* Sherrick, *J. Ind. Eng. Chem.*, **13**, 1011 (1921).
[8] *J. Ind. Eng. Chem.*, **12**, 138 (1920).
[9] *J. Phys. Chem.*, **19**, 245—46 (1919).

electrical methods, chemical methods, and mechanical or physical methods. Numerous patents exist in each case, and only the broad outlines of the best schemes employed to-day will be considered.

Electrical methods are based on the fact that coalescence of the water globules may follow the passage of an electric current (direct or alternating) through the emulsion. High potential alternating current is usually employed. F. G. Cottrell took out the pioneer patent[1] in this connection, claiming that the water particles " are subject to electrostatic forces dependent upon the relative potentials and dielectric constants of the materials in contact and caused to coalesce into masses " easily removed by settling or centrifuging. Braley[2] mentions that emulsions holding even 65 per cent. water have been economically dehydrated to 0·5 per cent. water and refuse by this process.

The " electrical dehydration " process has been described by W. G. and H. C. Eddy.[3] A galvanised steel tank (the " electrical treater "), approximately 3 feet in diameter and 8 feet deep, is provided in the centre with a vertical shaft carrying a number of circular discs. The shaft is mounted on an insulated bearing and slowly rotated. The tank shell is earthed and acts as one electrode ; the shaft acts as a revolving electrode, and a potential difference of 11,000 volts (alternating current and of any commercial frequency) is maintained. The oil-field emulsion is fed continuously into and through the annular electrical field so produced between the tank shell and the disc edges, whereby de-emulsification ensues. The freed oil and water pass into a settling tank, where separation is completed into oil and water (containing dissolved salts). A plant operated from a single circuit and motor may consist of any number of treaters from 1 to 8 in even multiples, also in banks of 6 units each. The capacity per treater averages from 300 to 1,000 barrels of oil per day, the character of the emulsion being an important factor in this respect. The consumption

[1] U.S. Pat. 287115 (1911).
[2] *Trans. Amer. Electrochem. Soc.*, **35**, 209 (1919).
[3] *J. Ind. Eng. Chem.*, **13**, 1016 (1921).

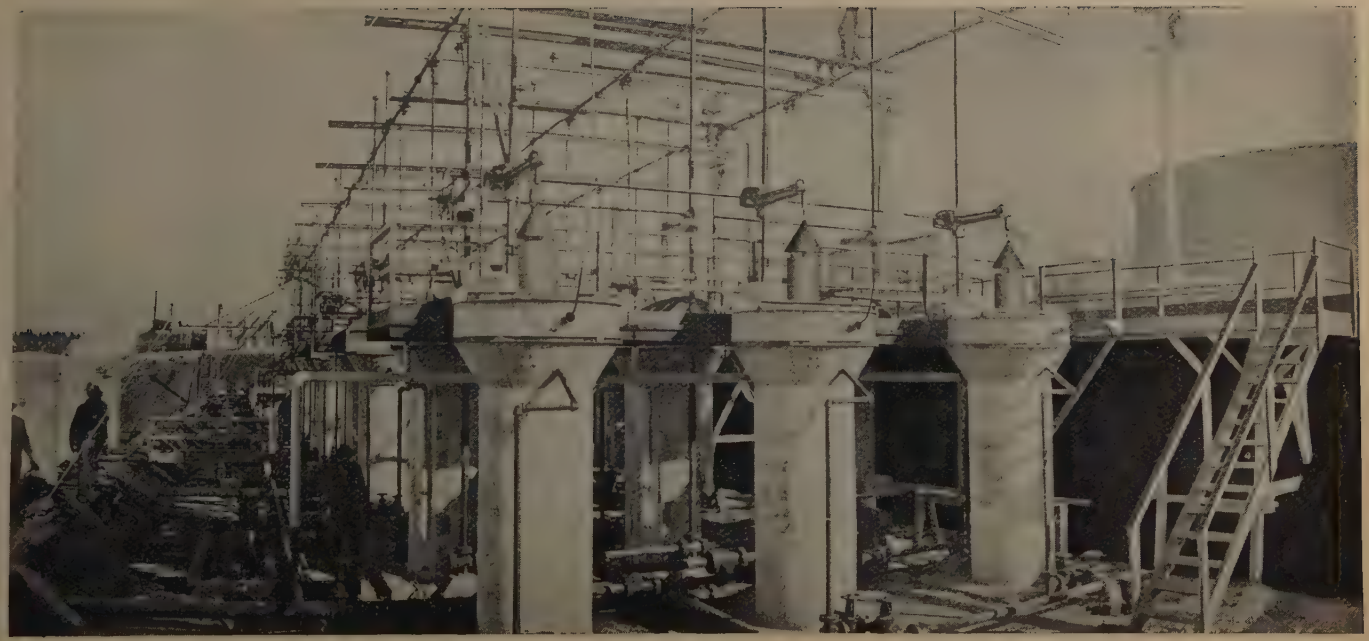

FIG. 19.—Electric Dehydrator Installation.

To face p. 127.

of electric power ranges from 5 to 75 watt-hours per barrel of dehydrated oil, the average cost of electricity (1921) being one cent. per 20 to 25 barrels. Where possible the plant is located so as to secure a gravity flow from the supply tank through the treaters and trap to the shipping tanks, requiring a minimum of piping and pumps. Fig. 19 shows a 30-unit installation at Orcutt, California, in 1920, dehydrating 12,000 barrels per day of a most troublesome emulsion containing 40 per cent. of water.

The maximum efficiency depends upon an optimum working temperature. The average temperature maintained is 57° C., but particularly stable emulsions may have to be raised to about 82° C. before treating electrically. With oils containing volatile constituents an enclosed type of heater becomes necessary. An extension of this method has been made by McKibben,[1] who proposes to pass the emulsion, heated to produce the vaporisation of the water, through an intensified electric field. The vapours are condensed and cooled, and the water separated off.

The theory underlying the Cottrell process and its modifications is that the emulsion serves as a multitude of electrical condensers, the electrodes or poles being the water globules and the continuous oil phase serving as the dielectric. Under the influence of a high-potential alternating field the charged water particles rupture the enveloping oil films and coalesce, forming larger drops. According to W. G. and H. C. Eddy,[2] who followed such a test by the aid of the micro-photographic cinema film, " this action of stress and strain, attraction and repulsion on the conducting water particles continues until all the microscopic drops of water in the original emulsion have broken the bonds of the entrapping oil films, the larger droplets serving as nuclei until the entire water content is freed into large drops which readily settle out."

Fig. 20 shows sections from a micro-photographic cinema film (made by W. G. and H. C. Eddy) taken four per second and magnified fifty times. Each section contains four indi-

[1] U.S. Pat. 1299590 (1919).
[2] *J. Ind. Eng. Chem.*, **13**, 1016 (1921).

vidual pictures. The first section shows the untreated emulsion, with 35 per cent. water as internal phase. The succeeding sections show the continued coalescence into a few large drops of the water globules under the influence of the electric current. The change can be clearly followed from one section to the next; particularly noticeable is the chain started from the larger water globules that happened to be somewhat lined up in the crude emulsion. The large water drops, as shown in the completed section, are now in a condition to settle freely to the bottom by gravity, and clear water can be automatically drawn off in a continuous stream.

The use of direct current has been patented by Seibert and Brady.[1] The method is based on the principles of cataphoresis. A voltage of 250 to 600 volts is employed, and the current varies from a few milliamps to 10 amps. This process, however, finds only a very limited application, though the Gulf Production Company embody it in their "combined method" for dehydrating oils in the Goose Creek (Texas). They employ a combination of closed heating, settling, direct-current electrical treatment, and centrifuging. The evaporation loss is very small, and the fuel consumption low. McKibben [2] has devised a process wherein a continuous uninterrupted, uniform electric field is maintained between electrodes with a conduit constituting a relatively long path, to polarise the water globules tending to chain formation, and the emulsion is passed through the field slowly enough to break up or prevent persistence of chains of polarised globules of entrapped water between the electrodes. Separation into oil and water is thus effected. A very similar idea underlies a patent by Harris.[3] Electrodes in the emulsion are caused to approach each other sufficiently to lead to formation of water chains between the electrodes, through which heavy short-circuit currents can flow. The electrodes are then separated and the current interrupted, whereupon water settles out.

Chemical methods for the de-emulsification of crude petro-

[1] U.S. Pat. 1290369 (1919).
[2] U.S. Pats. 1299589 (1919) and 1304786 (1919).
[3] U.S. Pat. 1281952 (1918); cf. also Laird and Raney, U.S. Pats. 1116299 (1914), 1142760 (1915), 1142761 (1915).

FIG. 20.—Micro-Photographic Cinema Record of the "Cottrell" Electric Dehydrating Process.

To face p. 128.

leum emulsions have found wide application, and present much variety. The essential principle involved is that, when an emulsion of water in oil is stabilised by an oil-soluble (hydrophobe) colloid, the addition of a suitable water-soluble (hydrophile) colloid can bring about coalescence. Academically such a scheme has been made familiar by Clowes [1] in his experiments on antagonistic electrolytes, which we have already discussed (*vide* p. 76).

Water-soluble soap is a common agent employed in the chemical treatment of emulsions. Sodium and potassium soaps are soluble in both water and oil, but according to Fischer,[2] the aqueous solutions of these soaps contain hydrated colloid, which is no longer soluble in oil. Sodium oleate is the basis of several patented compounds, *e.g.*, "Tret-o-Lite," which contains—

	Per cent.
Sodium oleate	83·0
Sodium resinate	5·5
Sodium silicate	5·0
Phenol	4·0
Paraffin	1·5
Water	1·0
	100·0

Matthews and Crosby [3] describe tests made with this mixture; they found that a 1 per cent. aqueous solution of "Tret-o-Lite," added to the emulsion in the ratio of 0·1 to 1·0 per cent. by weight, caused separation following upon agitation, and subsequent settling; working at a temperature of 65° C., expedited the de-emulsification.

Sometimes the crude oil emulsions can be "broken" by merely agitating with sodium carbonate. This is due to the formation of sodium soaps (acting as hydrophile colloids) formed by the reaction between the alkali added and the fatty acids present in the oil. The use of sodium salts of sulphonated

[1] *J. Phys. Chem.*, **20**, 407 (1916).
[2] *Science*, **43**, 468 (1916).
[3] *J. Ind. Eng. Chem.*, **13**, 1015—1016 (1921); cf. Gill, Brit. Pat. 180447 (1921).

mineral oils has been patented by Francis and Rogers,[1] who advocate the addition of such agents to the heated emulsions. De-emulsification readily follows such treatment. In this connection it is of interest to note that Levinstein has patented as emulsifying agents, for emulsions of oils, fats and waxes in water, sulphonated stearic acid[2] and sulphonated palmitic acid.[3]

Of other hydrophile colloids recommended in the de-emulsification of crude oils may be mentioned gelatin (glue) and starch. It is possible to prepare a concentrated gelatin mixture in fuel oil, which readily " breaks " these emulsions. Starch added in suitable oil-soluble form also acts very effectively, although starch is not usually considered a strong protecting colloid for oil-in-water emulsions. In a discussion of the use of these reagents it has been pointed out by Ayres[4] that " nothing of value can be said in regard to the percentages of such hydrophile reagents required to break these emulsions, because, in practice, the effects of the reagents are progressive. Taking, for example, an emulsion which can be separated in a given continuous centrifugal at the rate of five barrels an hour, the addition of 0·001 per cent. of oil-soluble sodium soap, glue, or starch, several hours before centrifuging will cause the rate of separation to be increased to fifteen barrels an hour. The same increase may be obtained by the addition of 0·01 per cent. of hydrophile colloid thirty minutes before centrifuging, or the addition of 0·1 per cent. at the time of centrifuging. Within practical limits, the more reagent is used the further will coalescence proceed in a given time. An absurdly small percentage of hydrophile colloid is enough to insure complete coalescence by contact if the emulsion is given time to come to equilibrium." From this one infers that the stabilising power of the hydrophobe colloid in oil-field emulsions must be low. The unexpected efficiency of starch certainly demands inquiry, particularly in view of the results of the present writer, who found the addition of starch in small quantities an excellent

[1] U.S. Pat. 1299385 (1919); *vide* also Matthews and Crosby, *loc. cit.*, p. 1015.
[2] U.S. Pat. 1176378 (1916).
[3] U.S. Pat. 1185213 (1916).
[4] *J. Ind. Eng. Chem.*, **18**, 1013 (1921).

means for flocculating certain very stable suspensions of inorganic solids in acid and alkaline liquors.[1]

An interesting case of de-emulsification of water-gas tar emulsions and oil-field bottom settlings has been mentioned in connection with the Trent process of "cleaning" coal.[2] The addition of finely-pulverised coal will "break" such emulsions, owing to the fact that oil wets coal much more than does water, whereby the reverse type of emulsion is promoted, leading to a breakdown of the system.

Coalescence by Electrolytes.—By adding suitable electrolytes to oil-field emulsions the charge on the water globules is neutralised and coalescence results. Such a scheme also appertains to emulsions of the oil-in-water type, as was shown by Hatschek.[3] Bottars [4] has patented the use of acids for the separation of oil-in-water emulsions.

Investigations by Sherrick [5] on the adsorption of H ion when acids were added to oil-field emulsions showed that the concentration of hydrogen ion necessary to effect complete discharge of water from the oil ranged around the value 10×10^{-1} normal. His method was to place 200 c.c. of emulsion, containing 25 per cent. of water, in a 500-c.c. ground-glass-stoppered graduated flask and add 50 c.c. of acid solution. After being shaken twenty minutes in an electrically-driven shaker, the flask was stood for twenty-two hours, when the percentage of water in the oil layer was determined.

Much better results were obtained by Sherrick, using ferric chloride solutions, from which ferric ion adsorption took place, resulting in separation of the emulsion. The $FeCl_3$ solution contained 66·24 grs. $FeCl_3$ per 100 c.c. To 200 c.c. of emulsion were added this solution and water, and the mixture shaken as before. It was found that with low concentrations of ferric ion the de-emulsification was perfectly regular; with higher concentrations, however, there was not a separation of the water phase itself, but jellies of varying stability resulted. It

[1] Clayton, in "Physics and Chemistry of Colloids" (H.M. Stationery Office, London, 1921), p. 119.
[2] *Chem. Met. Eng.*, **25**, 187 (1921).
[3] *Koll. Zeits.*, **9**, 159 (1911).
[4] Norw. Pat. 26667 (1916).
[5] *J. Ind. Eng. Chem.*, **13**, 137 (1920).

was found that these jellies contained positively-charged particles, the adsorption of ferric ions having carried the particles past the iso-electric point.[1] The following table shows the quantitative results obtained (at 25° C.) :—

Added Mixture.		Specific Gravity of Added Mixture	Water in Oil Layer after Twenty-two Hours' Standing.	Remarks.
$FeCl_3$ Solution. c.c.	Water. c.c.			
2·5	48·0	—	22·0	—
5·0	45·0	—	8·0	—
7·5	42·5	—	2·0	—
10·0	40·0	1·0610	1·5	150 c.c. black jelly with layer of good oil above. Unstable.
20·0	30·0	1·1213	1·5	125 c.c. black jelly. Unstable.
35·0	15·0	1·2050	0·5	180 c.c. stable stiff black jelly. Good oil on top.
50·0	0·0	1·2878	0·5	

It was found that a saturated solution of sodium nitrate immediately destroyed the jellies, owing to the strong adsorption of the NO_3 ion. It followed from this that a solution of ferric nitrate should precipitate the original emulsion without

Emulsion. c.c.	Added Mixture.		Separated.		Water in Oil Layer. Per cent.	Colour after Twenty-two Hours' Standing.
	$Fe(NO_3)_3$ Solution. c.c.	Water. c.c.	Solution. c.c.	Sponge. c.c.		
200	5	45	5	None.	32·0	Light brown.
200	10	40	15	70	16·0	Brown.
200	15	35	25	80	5·0	Dark brown.
200	25	25	65	35	1·0	Dark brown.
200	50	0	65	35	0·5	Green-black.

Temperature = 25° C.
Ferric nitrate solution = 67·32 grs. $Fe(NO_3)_3$ per 100 c.c.

[1] Cf. Ellis, *Zeits. phys. Chem.*, **89**, 145 (1914).

intermediate jelly formation, since the adsorption of ferric ion would counteract to a certain extent the effect of the NO_3 ion. The table on page 132 illustrates results obtained by the simultaneous adsorption of ferric and nitrate ions on the emulsion. A spongy mass separated out, but this was very mobile and easily broken. Sherrick concludes that these results "clearly show that both ions have an effect in the precipitation."

Salting out Emulsions.—Undesirable industrial emulsions are sometimes "broken" by addition of common salt, which, when present in sufficient concentration, "salts out" the stabilising film surrounding the emulsion globules. Very little academic work has been done in this field, but a recent paper by Parsons and Wilson [1] indicates the kind of results obtained. "Nujol" (purified mineral oil) was emulsified in aqueous sodium oleate solutions, keeping the volume ratio constant, viz., 0·5, and NaCl, NaI, and Na_2SO_4 were added in varying concentrations. The salting-out effect causing de-emulsification was found to depend on the concentration of the added salt, and not on the ratio of the inorganic salt to sodium oleate. The table on p. 134 shows the effect of adding NaCl to "Nujol" emulsions.

Similar results obtained with NaI and Na_2SO_4. Varying the anion somewhat affects the salting-out capacity, since the minimum salting-out concentrations in equivalents were: $Na_2SO_4 = 0{\cdot}24$; $NaCl = 0{\cdot}22$; $NaI = 0{\cdot}18$.

The general principle underlying "salting out" of emulsions, as well as the inversion of phases in emulsions (see p. 97), is that the added reagent must be soluble in the external phase, or more easily wetted by it, so as to be able to influence the properties of the stabilising film.

Parsons and Wilson [2] hope to utilise the salting-out effect of NaCl in emulsions in order to determine quantitatively the emulsifying capacity of various emulsifying agents. The value sought is the equivalent concentration of NaCl necessary to break a given emulsion. Though only an arbitrary test of

[1] *J. Ind. Eng. Chem.*, **13**, 1120 (1921).
[2] *Loc. cit.*, p. 1121.

stability, it served to give good results in the case of "Nujol" emulsions.

Condenser Water Emulsions.—An important engineering problem has arisen in connection, more particularly, with forced lubrication in steam turbines. When steam passes through the valve chest and cylinder of an engine, particles of lubricating oil are carried along in a state of very fine subdivision, so fine, in fact, as to lead to the formation of emulsified oil when the

Equivalent Concentration.		Ratio B/A.	External Phase in Final Emulsion.	Remarks.
Sodium Oleate (A).	NaCl (B).			
0·0173	0·48	27·7	None.	Broke immediately.
0·0200	0·40	20·0	,,	,, ,,
0·0240	0·28	11·7	,,	,, ,,
0·0253	0·24	9·1	,,	,, ,,
0·0253	0·24	9·1	,,	,, ,,
0·0259	0·22	8·5	,,	Broke after some time.
0·0259	0·22	8·5	,,	,, ,,
0·0266	0·20	7·5	Water.	Creamed to two layers.
0·0266	0·20	7·5	,,	,, ,,
0·0280	0·16	5·7	,,	,, ,,
0·0120	0·14	11·7	,,	,, ,,
0·0293	0·12	4·1	,,	,, ,,
0·0307	0·08	2·5	,,	,, ,,
0·0320	0·04	1·25	,,	,, ,,
0·0333	*Nil.*	*Nil.*	,,	,, ,,

steam is condensed. Condensed water, in such cases, is milky, and the entrapped oil is present as an exceptionally stable emulsion, the oil particles being from 0·0006—0·00006 cm. diameter and negatively charged. Philip [1] has pointed out that mineral oils will emulsify in distilled water to a low concentration, but not in the presence of electrolytes, and we have already noted that the emulsifying capacity of mineral oils has to be determined before their suitability for lubricating purposes can be definitely established.

[1] *J. S. C. I.*, **34**, 697—701 (1915).

Condensed water emulsions are of great interest, inasmuch as mechanical, chemical and electrical methods have been used for separating the oil, owing to the value of the distilled water for boiler feeding and other purposes demanding chemically pure water.

Under the mechanical methods prior mention must be made of Hatschek's scheme.[1] In this it is proposed to coat the filtering surface of any suitable type of filter (*e.g.*, filter press) with a layer of calcium carbonate [2] of thickness depending on the rate of filtration per unit filtering surface, the percentage of emulsified oil, and the pressure used in filtering. Clear water passes through such a filter, the oil being retained on the surface of the chalk layer. Undoubtedly, the main factor operating in this filtration is not the size of the pores, but the fact that water wets calcium carbonate more readily than does oil. Emulsions of the water-in-oil type can be separated in a similar manner, viz., by passing the emulsion through a filter which is more easily wetted by oil than by water. Thus, when a crude petroleum oil-field emulsion is passed through powdered vulcanised rubber or iron sulphide, clear oil passes through, the water being retained at the filtering surface.

The Hatschek method is now superseded by chemical and electrical "de-oiling" devices. Advantage is taken of the fact that the oil globules are negatively charged, and can therefore be caused to coalesce by addition of a suitable electrolyte with a cation of high valency. Commercial sulphate of alumina is most commonly employed.[3] This salt contains on the average 53 per cent. of $Al_2(SO_4)_3$, equivalent to 16 per cent. Al_2O_3. The reagent is run into the condensed water together with sodium carbonate or caustic soda, whereupon a gelatinous precipitate of $Al_2O_3 \times (H_2O)_n$ is formed which unites with the oil globules so that these now become easily filtered. Careful regulation of the alkali is required to avoid redissolving the precipitate.[4]

[1] *J. S. C. I.* **29**, 125—128 (1910).
[2] Eng. Pat. 26228 (1908); cf. also Trumble, U.S. Pat. 1304124 (1919).
[3] Jackson, "Boiler Feed Water" (London, 1919), p. 55; Paul, "Boiler Chemistry and Feed Water Supplies" (London, 1919), p. 189.
[4] Cf. Gail and Adam, Brit. Pat. 161942 (1921).

Other types of industrial emulsions are separated by the use of electrolytes, *e.g.*, HCl, H_2SO_4, $AlCl_3$, Cu_2Cl_2, $BaCl_2$, etc., the important factor being the concentration of electrolyte.

The various electrical systems in use for "de-oiling" condensed waters operate either on the principles of cataphoresis or a combined electrochemical scheme. Typical of the former is the method proposed by Dijxhoom,[1] who subjects the emulsion to a P.D. of 110 volts as it passes through the feed water-pipe. The Davis-Perrett[2] process is an excellent example of "de-oiling" by electrochemical methods. The condensed water is sent in a zigzag path between iron or steel electrodes arranged in a wooden tank, and an electrical current is passed. Iron is precipitated from the anode and entangles the oil globules, which coalesce to form rusty-coloured flakes. These are easily removed by a filter, leaving clear water practically chemically pure. By suitably arranging the electrodes the latest plants can operate so that only 0·1 of a B.T.U. (100 watts) are required to treat 1,000 gallons of condensed steam. The plant is simple, only a short time is taken in treatment, and the condensed steam may be treated at as high a temperature as desired (see Fig. 21).

Paul[3] mentions a milky emulsion of condensed steam containing 3·64 grains of oil per gallon. After the electrochemical treatment it was quite clear. Analysis of the oily deposit gave: hydrated ferric oxide = 43·58 per cent., oil = 54·52 per cent., water = 1·6 per cent. The ferric hydrate has in this instance entangled about one and a quarter times its weight of oil, corresponding to two and a half times the weight of iron electrically dissolved from the anode.[4]

Centrifugal Separation of Emulsions.—Both emulsions of the oil-in-water and the water-in-oil types can be separated into oil and water by suitable centrifugal treatment, which depends on the difference in specific gravities of the two phases. It is really an enhanced gravity settling, the gravitational force

[1] *Le Papier*, **22**, 53 (1919); cf. Fanto and Stritar, *J. prakt. Chem.*, **81**, 564—568 (1910).

[2] Covered by U.S. Pat. 783107 (1905) and Eng. Pats. 10874 (1902), 8175 (1903), and 26577 (1908).

[3] *Loc. cit.*, p. 192.

[4] *Vide* also Goodwin and Ellis, *Chem. Zeit.*, No. **81**, 724 (1910).

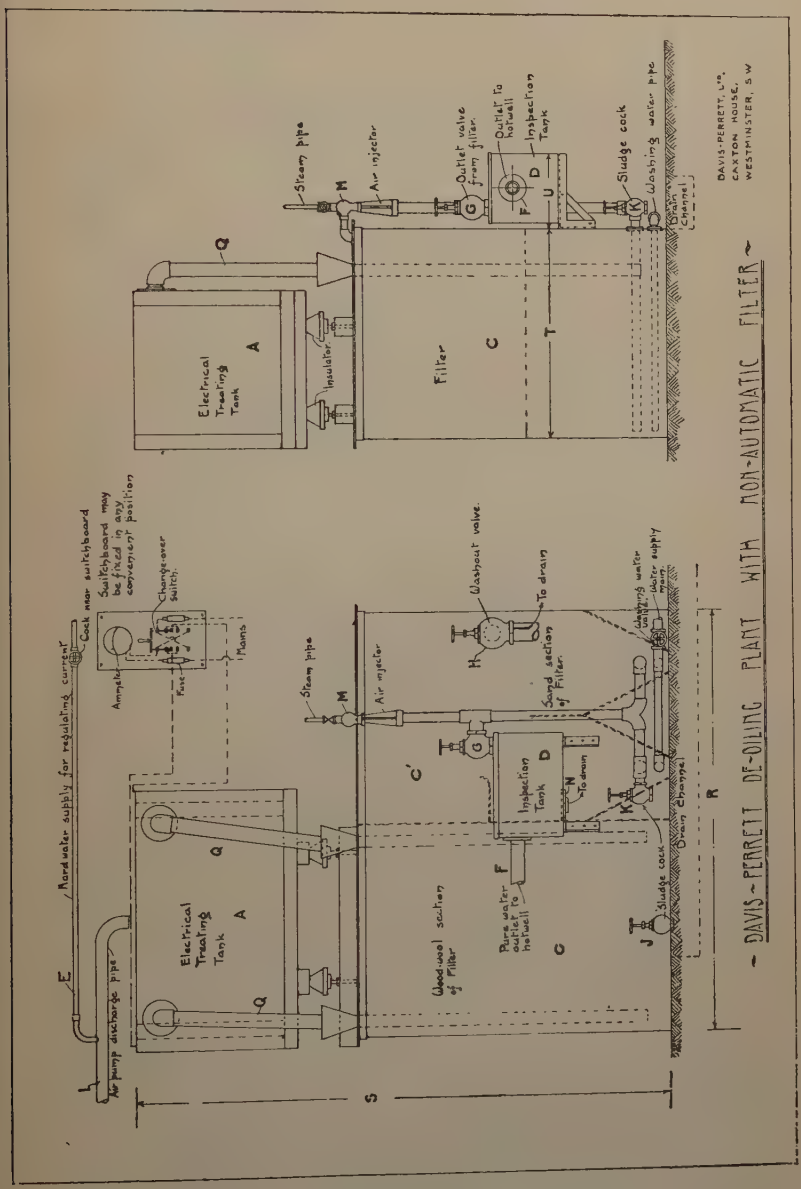
Hard water supply for regulating current
Cock near switchboard
Switchboard may be fixed in any convenient position
Change-over switch
Ammeter
Fuse
Mains
Air pump discharge pipe
Electrical Treating Tank
A
Q
E
L
S
Steam pipe
Air injector
M
Washout valve
To drain
Sand section of Filter
Inspection Tank
D
N
To drain
Drain Channel
Pure water outlet to hatwell
F
Woodwool section of Filter
C
C'
Sludge cock
J
K
T
R
Washing water supply main
Steam pipe
H
Air injector
Outlet valve from filter
G
Outlet to hatwell
Inspection Tank
D
F
U
Sludge cock
K
Washing water pipe
Drain Channel
Filter
C
T
Insulator
Electrical Treating Tank
A
Q
DAVIS-PERRETT, L.TD. CAXTON HOUSE, WESTMINSTER, S.W.
~ DAVIS-PERRETT DE-OILING PLANT WITH NON-AUTOMATIC FILTER ~

FIG. 21.

being enormously magnified. The dispersed phase moves through the dispersing medium with a velocity influenced by the following factors: (1) centrifugal force exerted; (2) viscosity of dispersion medium; (3) difference in specific gravity between the phases; (4) relation between the mass and the surface area of the globules; (5) temperature; (6) chemical nature of the phases.[1]

Stokes' law for the constant velocity of a small sphere falling in a liquid is given by

$$V = \frac{2r^2(S - S')g}{9\eta},$$

where r = radius of the globules.

s = specific gravity of dispersed phase.

s' = specific gravity of the dispersion medium.

η = viscosity coefficient of the dispersion medium.

g = the gravity constant.

From this equation it is obvious that, though the specific gravity difference is important, the importance rapidly diminishes when the diameter of the particle is sufficiently reduced, since the velocity is proportional to the square of the radius. With very small globules, and with but little difference between the specific gravities of oil and water, emulsions of great stability are possible, sometimes even defying centrifugal treatment. Other factors now have predominating effects, *e.g.*, electric repulsion, interfacial tension, and Brownian movements.

On the whole, industrial emulsions are always capable of being separated by centrifugal machines, since the emulsified particles are sufficiently large for such treatment. Frequently the viscosity of the dispersion medium is the main factor for consideration, and heat may be necessary before the more stable emulsions can be centrifuged. Sometimes a partial chemical or electrical coalescence must precede centrifugal separation.

Centrifugal separators date from about 1850, but the first continuous centrifugal separator was invented by Gustaf de

[1] *Vide* Ayres, *J. S. C. I.*, **35**, 676—680 (1916); *Met. Chem. Eng.*, **14**, 500—502 (1916); and *J. Ind. Eng. Chem.*, **13**, 1011—1013 (1921).

Laval in 1878, and was applied to the separation of cream from milk. Since the modern de Laval machine is employed in numerous industries with recognised efficiency, this type will be discussed in some detail as being typical of centrifugal practice. As a special case, its application to cream separation may be taken.[1]

The essential part of the machine is the bowl, capable of being revolved at high speed, containing a series of round, sloping, conical steel discs, superimposed and spaced slightly apart by thin calks or ribs fastened to them. Milk is fed into the centre of the bowl by a distributing device contained in the central shaft, and passes through tangential slots in the wall of the shaft into enclosed gutters. It now flows from the lower ends of these gutters (which extend beyond the cream wall), and is delivered into the neutral zone or separating disc space of the bowl, passing upward into the various discs through a series of openings in the discs located above and in line with the distributing device outlets. The important result is thus obtained of delivering the incoming milk into the separating discs without interference of the cream wall or mixing of the incoming milk with the already separated cream. The separation then takes place in the discs, the cream particles moving inward toward the centre and forming the cream wall round the central shaft and distributing device and mounting upward to the point of discharge through the cream outlet. The skim-milk moves outward beyond the discs and is carried upward along the wall of the bowl to the points of discharge through the skim-milk outlets (see Fig. 22).

It can be shown [2] that under the influence of centrifugal force the time required for a globule of radius r to travel through a given space is proportional to the square root of the cube of the radius, *i.e.*, $r^{\frac{3}{2}}$. As the number of gallons of emulsion (milk) dealt with per hour by the separator is inversely proportional to the time, it follows that for any given radius of globules there is a critical value where its velocity against the stream of milk will be equal to the velocity of the stream itself,

[1] *Vide* O. Hunziker, "The Butter Industry" (1920), pp. 70—102; W. A. Stocking, "Manual of Milk Products" (1917), pp. 229—235.

[2] Richmond, "Dairy Chemistry" (1914), pp. 255—259.

so that globules of smaller radius pass out with the stream or separated milk. The fat content of the separated milk is proportional to the cube root of the square of the number of gallons per hour.

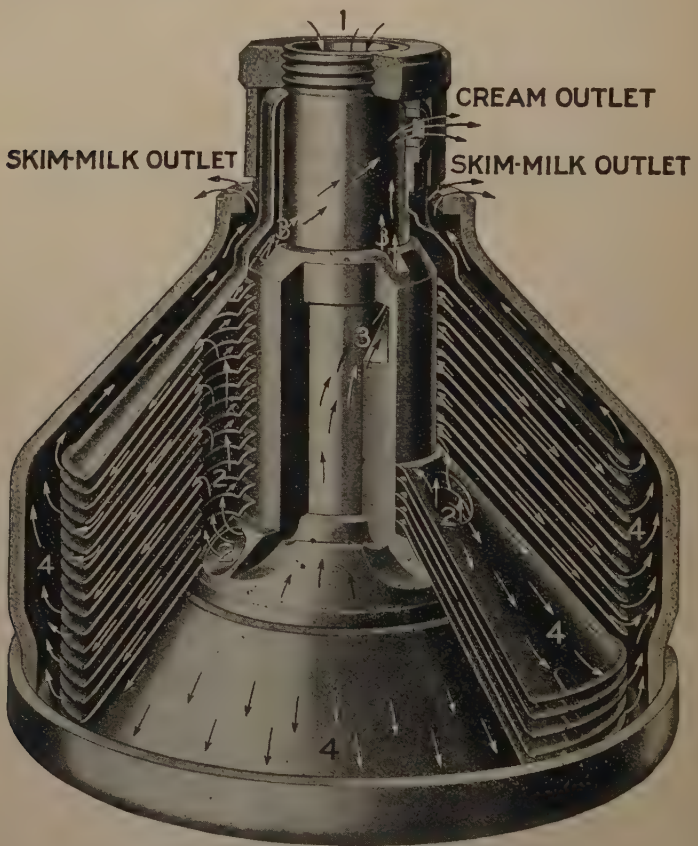

Fig. 22.—Cross-Section of De Laval Cream Separator.

Centrifugal machines for cream separation are usually run at 6,000 revolutions per minute. The intensity of the centrifugal force exerted is directly proportional to the mass of the contents of the bowl, to the diameter of the bowl, and to the square of the speed of revolution.[1] The ratio of cream to separated milk

[1] *Vide* Lamson, " A Study of Farm Separators " (Thesis. Purdue. Univ., U.S.A. (1918)).

will depend on the relative distances of their respective outlets from the centre of the bowl under normal running conditions. An important figure in cream separation is the " capacity " of the separator, *i.e.*, the amount of milk which can be separated per hour. Obviously, the capacity depends on the centrifugal force and on the rate of inflow of the milk. Any increase over the optimum capacity will lower the efficiency of the separator, since the milk will necessarily be subjected to centrifugal action for a shorter period ; this means a loss of butterfat, carried away in the separated milk. The rate of inflow of the milk requires careful control ; reduction of the rate below the normal value does not lead to increased efficiency of separation, and merely lengthens the time required.[1]

Other factors which affect the centrifugal separation of milk are the temperature and the richness of the whole milk. Cream is usually separated from the milk at 29° to 35° C. At lower temperatures the viscosity of the milk increases and the fat globules are influenced by the greater resistance offered to the centrifugal separation. Though the cream is richer, due to the slower passage of the milk through the machine, the loss is greater, since the separated milk contains more than the usual amount of fat. At about 20° C. clogging of the machine occurs, due to the great viscosity and the incipient churning of the milk and cream.

The quality of the milk is important. The richer it is in butterfat, the richer is the cream and the greater the loss in the separated milk. As an approximate guide, the percentage of butterfat in the cream is proportional to the fat content of the whole milk.[2] Milk containing impurities, or which is beginning to sour and contain curd, lowers the skimming efficiency, owing to the separation of slime in the machine, which impedes the passage of the cream and milk and leads to large fat losses.

Crude oil-field emulsions provide another interesting industrial application of centrifugal separation. Many American centres still prefer this method of separation to electrical

[1] Hunziker, Purdue Agric. Expt. Statn., *Bull.* **116** (1906).
[2] *Vide* Guthrie, Cornell Univ. Agric. Statn., *Bull.* **360** (1915).

dehydration. Ayres [1] has pointed out that centrifugal separation has two related advantages over simple gravity settling. Firstly, "if the centrifugal force is from 15 to 18 thousand times as great as the force of gravity, the gravity separation will take 15 to 18 thousand times as long as the centrifugal. The emulsions in Kansas, Oklahoma and some parts of Texas require the exertion of a force of this magnitude to effect subsidence in 1 inch layers during a period of from 6 to 18 seconds. The corresponding figures for gravity are from 24 hours to 3 days." The second advantage is that, owing to the enormous reduction in the time required for subsidence, an emulsion may be heated for this brief period at a permissible cost, so enhancing coalescence at the higher temperature as to yield all the water as a homogeneous phase. Sometimes, instead of heating the original emulsion, it is first centrifuged at ordinary temperatures, and then the effluent (concentrated) emulsion is heated to cause coalescence prior to further centrifugal separation.

In passing, it is of interest to note that, when colloidal suspensions of the hydroxides of iron and aluminium are centrifuged, the initial impact of the colloid on the rapidly revolving bowl may so reduce the size of the particles as to lengthen the time required for centrifugal separation to a great degree. Ayres [2] mentions the case of a pyroxylin lacquer containing a fine cloud of cellulose impurities, which "cleared" on long standing by gravity alone. Centrifugal separation was impossible, the cellulose flocks being too unstable and too readily broken up.

Recently the super-centrifuge has been introduced into oil-field practice.[3] A frame supports a small high-speed turbine with a vertical shaft and one bearing, a cone, resting on ball bearings. The revolving bowl is about $4\frac{1}{2}$ inches in diameter, and is suspended from the turbine by a vertical shaft or spindle, thus securing direct transmission of power. The bowl is of a

[1] *J. Ind. Eng. Chem.*, **13**, 1011 (1921); cf. also *Chem. Met. Eng.*, **22**, 1057—1062 (1920).

[2] *J. S. C. I.*, **35**, 676—680 (1916).

[3] S. Born, *J. Ind. Eng. Chem.*, **13**, 1013 (1921); cf. Keable, *J. Oil Colour Chemists' Assocn.*, 5, 2—15 (1922).

special alloy steel, and special devices provide the maintenance of correct alignment during rotation at about 17,000 r.p.m. Besides possessing the advantage of greater speed and enhanced centrifugal force, the super-centrifuge permits a longer application of centrifugal force to the emulsion particles, owing to the elongated bowl. The emulsions are gravity-fed to the separator under a head of about 30 feet, being previously heated to 110° to 180° F. (43° to 82° C.). In starting up the bowl is revolved slowly and brine admitted until full speed is attained, when emulsion is run in continuously. About 100 to 200 barrels of dehydrated oil can be obtained from one machine in twenty-four hours. Even "bottom settlings" containing 70 per cent. to 80 per cent. of water can be cleared to oil containing as little as 0·5 per cent. water.

Heat Treatment.—In certain instances oil-field emulsions are "broken" by heating; especially is this the case with bottom settlings. The consequent lowering of viscosity of a heated emulsion aids separation, but care must be taken to avoid loss of valuable volatile products. The method recommended is to have a live-steam coil immersed in water, the emulsion resting above this and being heated by convection currents to 50° to 70° C. A battery of five tanks is often used, the heated emulsion flowing from the first tank into the second, being further heated there, and then flowing to a third. The fourth and fifth tanks are storage tanks, where settling takes place, the water (containing salts) being run off from time to time, thus permitting a continuous run of months.

Sometimes the emulsions are "broken" by means of a "topping plant," which embraces a distillation at 175° to 260° C. through pipe stills. Water passes on with the volatile oils and is readily separated on condensation. The method is well adapted for heavy oils, and is extensively used in California. A somewhat similar idea underlies the process of Krause,[1] in which the emulsion is atomised into a body of moving air, gas, or steam, both being moved in vortices in the same direction. Condensation is at once followed by separation of oil and

[1] Holland Pat. 2960 (1919).

water. The question of loss in heat dehydrators of emulsions has been discussed by Wiggins [1] and by Buck.[2]

Kammann and Keim,[3] discussing various methods of "de-oiling," state that oil refinery wastes can be almost completely separated into oil and water by heating under pressure, 4 to 5 atmospheres being the order required.

According to Pilat and Piotrowski,[4] crude petroleum emulsions may be broken by heating with steam at 3 to $3\frac{1}{2}$ atmospheres pressure (120° to 130° C.). The greater the pressure, the more rapid is the separation. A similar scheme is advocated by Koetschau.[5]

By centrifuging emulsions against heated plates, whereby the water is instantaneously evaporated, dry oil may be obtained.[6]

Whilst heating is used in technical practice for breaking certain emulsions, freezing has also been mentioned as a means of breaking stable emulsions, though but little work has been done in this connection. Newman [7] froze a stable homogeneous emulsion, containing 95 per cent. by volume of benzene in dilute sodium oleate solution. On thawing, the emulsion broke and could not be restored by shaking. The breaking of the emulsion was probably due to the rupture of the soap films around the benzene globules, but the irreversibility was probably only apparent and due to the very slow redissolving in water of the coagulated sodium oleate.

[1] *Nat. Petroleum News*, **13** (26), 59—65 (1921).
[2] *Oil and Gas. J.*, **20**, 80—81 (1921).
[3] *Gesund. Ing.*, **43**, 245—247 (1920).
[4] *Petroleum*, **13**, 1045 (1918).
[5] *Zeits. angew. Chem.*, **32**, 45 (1919).
[6] Ger. Pat. 273100 (1909).
[7] *J. Phys. Chem.*, **18**, 45 (1914).

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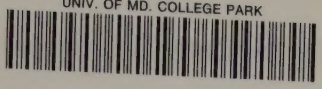

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